TECHNICAL MEMORANDUM #4: CONCEPTUAL MODEL OF SELENIUM IN NORTH SAN FRANCISCO BAY

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Prepared for
Regional Water Quality Control Board
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Executive Summary

North San Francisco Bay (NSFB) is identified as being impaired by selenium, principally due to elevated concentrations in fish and waterfowl. Selenium is a bioaccumulative substance, that is, it is sequestered to higher levels in the tissues of organisms in the bay than found in the water column or sediments. This memorandum presents a conceptual model of fate and transport of selenium in the NSFB and provides a summary of the processes that link selenium from various external sources to tissue concentrations that are of interest in the TMDL. The main features of selenium behavior in the water column, sediments, and biota are summarized below.

Water Column: Selenium enters NSFB in dissolved and particulate forms from the Delta, from point sources such as the refineries and municipal wastewater treatment plants, and from local tributaries. Both dissolved and particulate selenium can exist as different species that affect their cycling and bioavailability (selenate, selenite, organic selenides, and elemental selenium). Dissolved selenium can be taken up and bioconcentrated by algae and bacteria in the water column and add to the supply of particulate selenium. Selenite is the most bioavailable and bioaccumulative form of dissolved selenium. The exchange between selenate and selenite is slow, and is unlikely to occur significantly over the residence times in the bay. Conversion of selenite to organic selenide forms through microbial uptake is more rapid and is likely to be important in the bay.

Sediments: Depending on the flow rate and season, deposition to and erosion from the sediment bed can also be a sink/source of particulate selenium to the water column. Sediments are more reducing than the water column, and may result in conditions that reduce selenate and selenite to elemental selenium, Se (0), a form that is insoluble and less bioaccumulative than selenite.

Biota: Because of the preferential partitioning of some forms of selenium onto particles (both organic and inorganic), they are a comparatively rich source of selenium to organisms that consume them. Filter-feeding benthic organisms such as bivalves ingest and assimilate the particulate forms of selenium at different efficiencies depending on the type of particulate material. Direct ingestion of dissolved selenium is minimal for organisms besides phytoplankton and bacteria. Bivalves typically biomagnify selenium to concentrations higher than found in the particulate phase. When these organisms are consumed by predator species such as white sturgeon and diving ducks, the selenium is biomagnified further in the tissues of these animals. Algal and bacterial-associated selenium can also enter the food through a non-benthic pathway, i.e., through zooplankton that feed on these organisms, and through consumer organisms that feed on zooplankton. However, selenium concentrations in the non-benthic pathway are closer to background concentrations in the system.

Despite the mechanistic knowledge of selenium bioaccumulation developed, and summarized in this document, there are still many uncertainties in predicting future concentrations of selenium in tissues, given current or modified loads. The ability to estimate future selenium concentrations in various media in response to changing loads and/or other external factors is needed for the assimilative capacity determination for this TMDL. The areas and data gaps identified for further evaluation are:

1. **Chemical Speciation**. All available data on aqueous selenium concentrations since 1999 in NSFB are non-speciated selenium measurements. The likelihood of changes in the dissolved and particulate selenium concentrations and the chemical form of selenium in the aqueous phase from changes in the selenium sources to NSFB is substantial. The lack of these data is an important data gap.

2. **Phytoplankton Community Structure**. Laboratory data show the dramatic effect of algal species on selenium uptake. Changes in phytoplankton species composition in the bay change with season and over the years and the effect on the uptake of selenium needs to be quantified.

3. **Bivalve Populations**. There has been an increase in phytoplankton productivity to levels seen prior to the *Potamocorbula amurensis* invasion in the mid-1980s. In the recent past, it has been thought that the invasion of *P. amurensis* could adversely affect selenium levels in higher trophic levels because of the ability of *P. amurensis* to bioaccumulate it to higher levels than native species. Bivalves are a singularly important link in the observed bioaccumulation of selenium in fish and birds in NSFB. Changes in the abundance of *P. amurensis* and other bivalve species may affect the levels of bioaccumulation in the future. Additional information is needed on the size and distribution of *P. amurensis* and other bivalve populations.

4. **Bioaccumulation in Fish and Birds**. The impairment determination for NSFB is principally due to elevated selenium concentrations in fish and waterfowl, yet there are limited recent tissue concentration data on fish and avian species. Additional data on tissue concentrations by species and life stage needs to be collected.

1. Background and Purpose of Conceptual Model of Selenium for North San Francisco Bay

North San Francisco Bay (NSFB) is identified as being impaired by selenium, principally due to elevated concentrations in fish and waterfowl. This technical memorandum, one of a series of six, has been prepared in support of the selenium TMDL currently being developed by the San Francisco Bay Regional Water Board to address this impairment. Two prior technical memorandums have summarized water and sediment quality data and addressed the magnitudes of selenium sources to NSFB (TM-2) and the toxicological endpoints of concern with respect to species in NSFB (TM-3). This memorandum presents a conceptual model of selenium in NSFB and is identified as TM-4. The particular focus of this TM is on the processes that relate selenium load to the bay to concentrations in biota. Selenium occurs naturally at elevated levels in soils in parts of the watershed draining the NSFB; however anthropogenic activities, such as irrigation in selenium-rich areas and point sources, can add to the natural loads of selenium in the bay.

In the early stages of the TMDL development an important step is to determine the assimilative capacity of a pollutant in a water body. Assimilative capacity is used to define the ability of a water body to naturally absorb and use a discharged substance without impairing water quality or harming aquatic life. For the selenium TMDL, the applicable targets, yet to be determined, could take the form of water column or tissue concentrations. The sequence of steps that relate sources of selenium to the two types of endpoints, water column and tissue, are shown in Figure 1-1. Although represented in simple schematic form, the steps shown in Figure 1-1 may involve complex hydrodynamics, biotic and abiotic reactions in water column and sediments, and uptake and bioaccumulation through the food web. Bioaccumulation, defined as the sequestration and elevation of concentration of a chemical in the tissues of organisms, is an especially important process for selenium, because this element concentrates to much higher levels in tissues than is found in the water column.

(a)

(b)

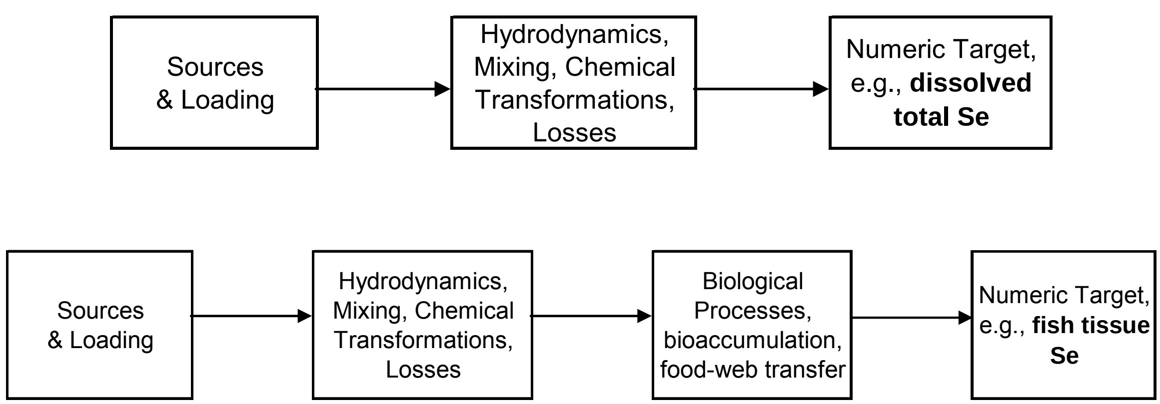


Figure 1-1 Sequence of steps relating sources of selenium to TMDL numeric targets, which may be (a) water column concentrations or (b) concentrations in biota.

Because the relationship between load and targets, and hence the determination of assimilative capacity, is complex, a conceptual model is often developed to capture the most important aspects of the relationship. For the purpose of this TMDL, the primary objective is to explain important selenium-related processes to stakeholders and to lay out broad areas of agreement in the scientific literature. Secondary objectives include the development of a summary of spatial and temporal trends in selenium data, with a focus on concentrations in bivalves, waterfowl and fish, so that they can be compared against toxicological and health-based guidelines; and guidance toward the development of a numerical model to link selenium sources quantified in TM-2 to numeric concentrations in water, sediments, and biota. The model can be used to evaluate changes in concentrations in response to changing selenium loads, and/or to other changes occurring in the NSFB ecosystem.

The focus of this conceptual model is on uptake processes that are currently well understood and quantified through measurements, and that may be represented numerically in a TMDL framework. Given the complexity of the food web in the bay, including the presence of migratory species, and the complexity of selenium behavior in the tissues of some of the species of interest, many aspects of selenium behavior are not fully quantified. These are acknowledged where appropriate, and may be addressed through adaptive implementation of the TMDL.

The region of interest for the NSFB selenium TMDL, and hence this conceptual model, consists of a portion of the Sacramento and San Joaquin River Delta, Suisun Bay, Carquinez Strait, San Pablo Bay, and Central Bay (Figure 1-2).

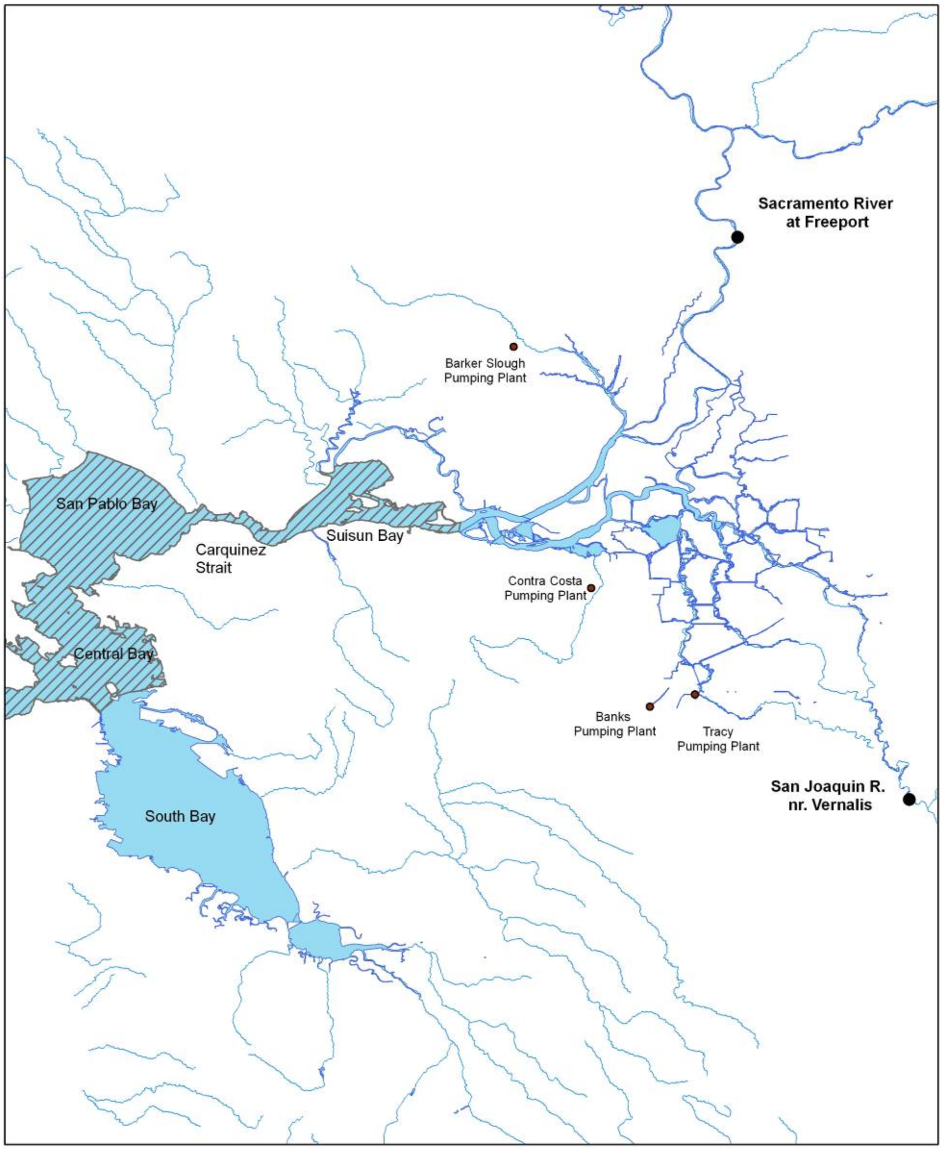


Figure 1-2 San Francisco Bay and surroundings. The cross-hatched area shows the area of interest for the North San Francisco Bay (NSFB) selenium TMDL. The Sacramento-San Joaquin River Delta is the primary source of freshwater inflow into NSFB. Significant volumes of freshwater are withdrawn for municipal and agricultural use from the Delta through the pumping plants shown.

2. Selenium-Related Processes in NSFB

Water column selenium concentrations in NSFB are relatively low, and the bay is thought to be impaired by selenium primarily due to the elevated concentrations in bivalves and organisms that feed on bivalves (Presser and Luoma, 2006). For this reason, it is critical to identify the processes that link low water-column concentrations to high concentrations in the tissues of specific organisms of concern, such as white sturgeon and diving ducks (surf scoter and scaup).

The mechanisms and intermediate steps that relate various selenium sources to elevated tissue concentrations in selected species are shown schematically in Figure 2-1. These processes have been elucidated through laboratory and field research over the past three decades and the combined knowledge is summarized below:

- Selenium enters NSFB in dissolved and particulate forms from the Delta, from point sources such as the refineries and municipal wastewater treatment plants, and from local tributaries. Quantitative estimates of these sources are those presented in TM-2. Atmospheric deposition and loss are poorly quantified and not thought to be very significant in the NSFB.
- Most of the selenium entering the bay is in the dissolved form, with a small fraction (10% or less) in the particulate form.
- Both dissolved and particulate selenium can exist as different chemical forms (or species) that affect their cycling, interchange, and bioavailability.
- Dissolved selenium can be taken up and sequestered by algae and bacteria to a level hundreds or thousands of times higher than concentrations in the water column. This process of direct uptake from the water column is called *bioconcentration*, and is the first step in the *bioaccumulation* of selenium in the food chain.
- Erosion from the sediment bed, upstream riverine sources, and uptake by algae/bacteria are the main sources of particulate selenium in the water column.
- Particulate selenium, whether as part of algal tissue, or associated with organic or mineral matter, is the form that is most likely to be taken up by organisms such as zooplankton, and benthic filter feeders such as bivalves.
- Filter-feeding benthic organisms ingest and assimilate the particulate forms of selenium at different efficiencies depending on the type of particulate material. Uptake of dissolved selenium is minimal for organisms besides phytoplankton and bacteria.
- Bivalves bioaccumulate selenium and typically magnify selenium to concentrations higher than found in the particulate phase (by a factor of 5-8). When these organisms are consumed by predator species such as sturgeon and diving ducks, the selenium is biomagnified further (3-19 times) in the tissues of these animals.
- Algal and bacterial-associated selenium can also enter the food chain through a non-benthic pathway, i.e., through zooplankton that feed on these organisms, and through consumer organisms that feed on zooplankton.

An understanding of the individual processes that result in elevated tissue concentrations are critical from the standpoint of the selenium TMDL. Two terms are commonly used to represent the aggregate result of the processes shown in Figure 2-1. The term *bioconcentration* refers to the elevated concentrations in tissue when the uptake occurs directly from the water column rather than through the diet. A more general term for the phenomenon of elevated concentrations in tissues is *bioaccumulation* and can refer to elevated concentrations through the dietary pathway, as well as through direct uptake. The ratio of tissue concentration to water column concentration (bioconcentration factor or bioaccumulation factor, BAF, expressed as L/kg) is often used to represent these processes and can be used to compare selenium behavior across trophic levels and across different types of water bodies. In NSFB, BAFs for algae can be ~25,000 L/kg, and for fish ~100,000 L/kg. These high values are the reason why tissue concentrations can be a problem even when water column concentrations are low.

The remainder of Section 2 describes the cycling of selenium in more detail, including the forms of selenium in the dissolved phase, the particulate phase, transport processes in the bay, the uptake by bivalves, and uptake by higher trophic level organisms. This discussion includes data from field and laboratory studies to illustrate and quantify various processes. Section 3 presents pertinent field data from NSFB for different environmental compartments, with a focus on temporal trends, to serve as a foundation for what might be expected in future.

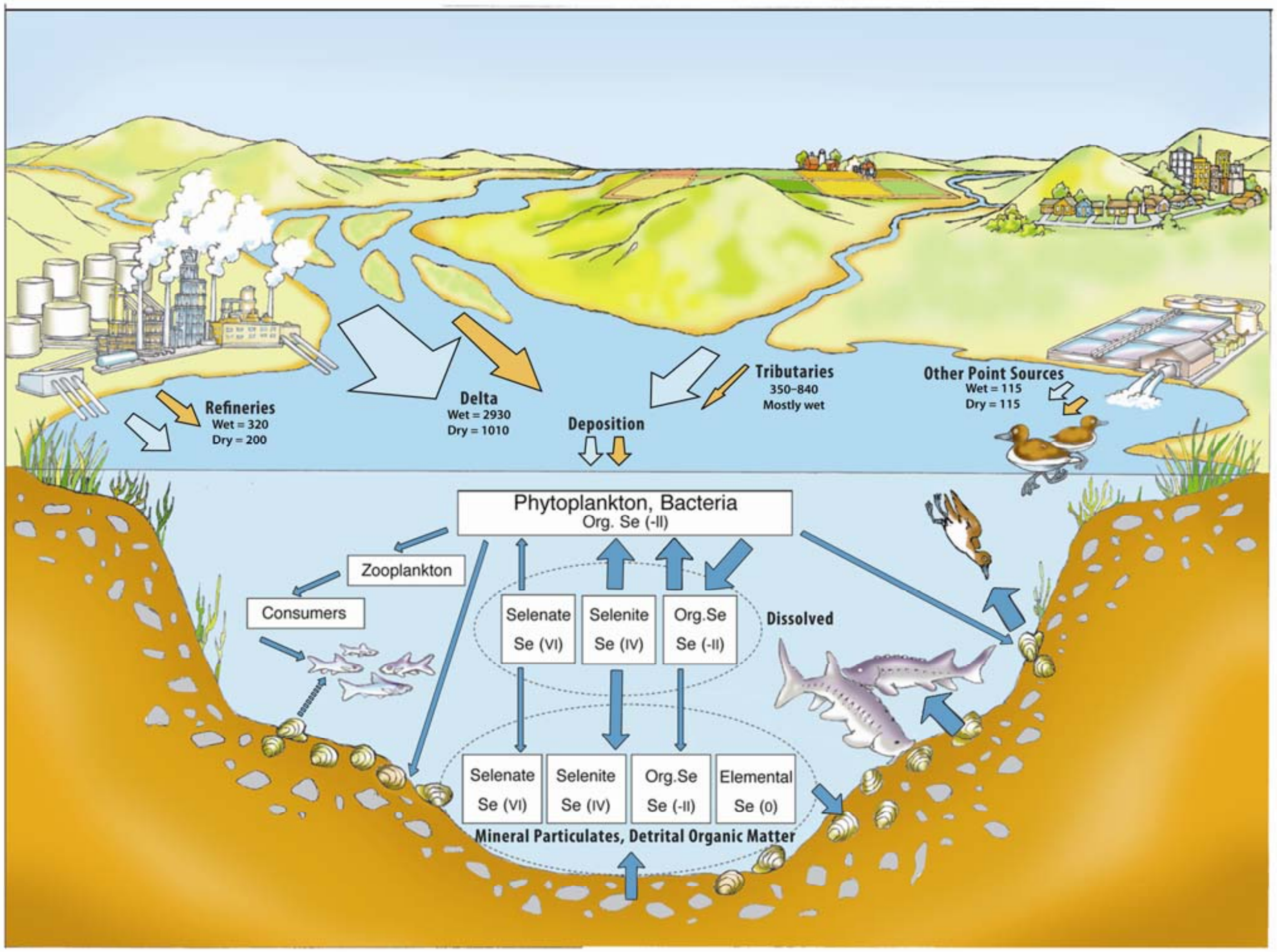


Figure 2-1 Selenium sources, cycling, and key pathways of bioaccumulation in NSFB (modified from Presser and Luoma, 2006; Bowie et al., 1996; Meseck and Cutter, 2006; and Abu Saba and Ogle, 2005). Load estimates are in kilograms for wet and dry seasons from TM-2 (blue arrows, wet season; brown arrows, dry season). Deposition loads are not specified because no local data exists. Selenium uptake into higher trophic level biota in primarily from the particulate phase, whether as phytoplankton and bacteria, or as detrital organic matter and suspended mineral sediments. Benthic organisms, such as bivalves, can accumulate high concentrations in tissue and serve as a major pathway for predators that are mostly dependent on the benthos for their food, such as white sturgeon and diving duck species (Greater and Lesser scaup and Surf Scoter).

2.1. SELENIUM IN THE DISSOLVED PHASE

Dissolved selenium exists in primarily three oxidation states, and each of those states is important to the fate and cycling of selenium, as well as its toxicity. A fourth oxidation state, elemental selenium, is mostly found in sediments or suspended particulate form. The common forms of selenium in the dissolved phase, shown in Figure 2-1, are:

- **Selenium (+VI) (selenate):** This form of selenium is present in very oxidizing environments, and does not adsorb strongly to particulates. Its uptake by organisms such as algae is less significant than uptake of selenite. In 1999, dissolved concentrations of selenate in the North Bay were approximately 0.06 µg/L to 0.08 µg/L (Cutter and Cutter, 2004). Sources of selenate to the Bay include refineries, municipal waste water discharges, delta inputs and loads from local tributaries.
- **Selenium (+IV) (selenite):** This form of selenium is a dominant species in oxygenated estuarine waters and can be a significant fraction of the total selenium present (Meseck and Cutter, 2006). It can be taken up by microbes and algae much more readily than selenate and partitions more strongly to particulates in general. In 1999 dissolved selenite concentrations in NSFB were approximately 0.02 µg/L (Cutter and Cutter, 2004). Sources of selenite to the Bay are similar to those of selenate. Before reduction in refinery loads in 1998, refinery inputs were a significant source of selenite to the Bay.
- **Selenium-II (selenide):** Selenides can form through the uptake of oxidized selenium by plankton, where the selenium is biologically reduced and incorporated into organic compounds. Under highly reducing conditions selenides are thermodynamically stable, and can bind to metals to precipitate as metal selenides. Also, methylated selenides can be formed, and volatilize to the atmosphere, although selenium volatilization in NSFB has not been quantified in any prior study. Even though NSFB waters are oxic, selenides are detected and reflect the outcome of rate-limited transformation processes. In 1999, concentrations of dissolved selenides were approximately 0.03 µg/L (Cutter and Cutter, 2004). A portion of the organic selenide originates in biological processes outside the Bay, as for selenate. However, an important additional *in situ* source of organic selenide is the uptake of selenite and selenate and transformation by plankton.

2.2. SELENIUM IN THE PARTICULATE PHASE

Particulate selenium may be operationally defined as selenium associated with material that can be filtered out of the water column. An understanding of particulate selenium chemistry is central to the conceptual model because this is the form that is taken up by bivalves and zooplankton and becomes available for bioaccumulation into higher trophic level organisms. Particulate selenium can exist in four distinct forms.

- **Mineral-particulate selenium:** Suspended mineral particles form the predominant fraction of the suspended material in the bay water column. Selenium can be adsorbed onto these particles as selenate, selenite, or organic selenide. Of these forms, selenite is the form that has the highest affinity for particles. Exchange between the water and sediments may be important source of mineral sediment-associated selenium. Riverine inputs from the Delta or from tributaries are also an important source. Data in the bay, and elsewhere, show that selenite has a much greater particle affinity than selenate.

- **Elemental selenium in zero oxidation state**: This form is stable in mildly reducing conditions, is very insoluble, and can be present in sediments or in suspended particulates. As sediments are re-suspended, elemental selenium can be oxidized in the water column to selenite where its cycling continues. In 1999, elemental particulate selenium concentrations in North Bay were approximately 0.003 µg/L (Cutter and Cutter, 2004).
- **Algal or bacterial associated selenium:** Selenium species, particularly selenite, can be taken up into the cytoplasm of these unicellular organisms as be converted into various organic forms such as seleno-methionine. Concentrations in algae or bacteria vary by species and by ambient selenium concentrations. Selenium in these particulate forms is most available for uptake by filter feeding bivalves. Upon respiration, these algae and bacteria release selenium in the form of organic selenide, which may be oxidized to selenite or taken up again by new growth.
- **Selenium associated with organic detritus:** Selenium may be associated with non-living particulate organic carbon, which is likely to have originated in biologically associated selenium. Organic-associated selenium may originate in sediments or from the death or organisms in the water column.

2.3. TRANSPORT OF SELENIUM IN THE NORTH BAY

External forces that have a major influence on the transport of selenium in the bay are, to a large degree, uncontrollable by humans, but must be accounted for to adequately model behavior under a range of conditions. The major drivers, illustrated in Figure 2-2, are tidal forcing (including sea level rise if long term trends are to be considered), meteorological forcing, hydrologic forcing, and winds. The bathymetry also has a great influence on how the water flows within the Bay, on sediment transport, on flushing, and ultimately on the fate of selenium.

As shown in Figure 2-2, tidal forcing is manifested by tides that enter San Francisco Bay through the Golden Gate. Example time series of tidal elevations are illustrated for two time periods: three days and thirty days. Multiple tidal frequencies (or multiple tidal periods) exist that originate from astronomically generated forces. Over a time period of several days, the semi-diurnal and diurnal nature of the tides is evident. Over a time period of approximately one day, two high tides of unequal height and two low tides of unequal height occur. The tidal cycle continues to evolve throughout the month, also shown in the figure, as spring and neap tides occur. Spring tides are those tides that are associated with the largest tidal amplitude, and neap tides are associated with the smallest amplitudes. Increased tidal flushing is associated with spring tide conditions, and minimal flushing is associated with neap tide conditions. These conditions affect the flushing of selenium that originates in NSFB. Over a time frame of many decades, sea level rise at the Golden Gate can slowly raise the average level of the bay. This can produce less flushing, and increase salinity intrusion.

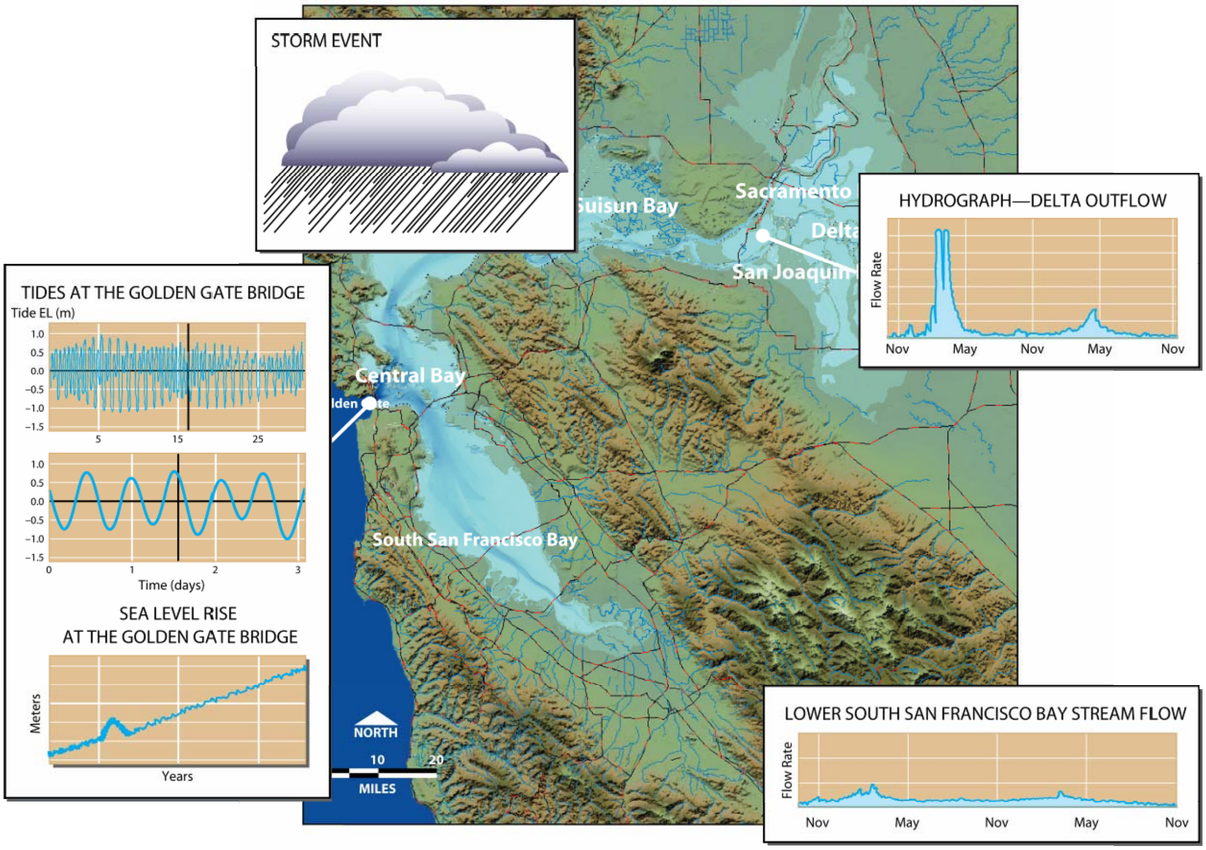


Figure 2-2 Illustration of tidal, freshwater and meteorological forcing functions.

Freshwater enters San Francisco Bay primarily through the Delta and through local streams. As might be expected due to the larger sizes of the watershed that feeds the Delta, these flow rates are typically orders of magnitude higher than local inflow rates. The residence times of constituents in the waters of NSFB are as little as a week during high flow conditions to more than a month for low flow conditions.

The hydrographs are strongly seasonally variable, with peak flows from the Delta occurring during the wet season, and into spring when snowmelt from the distant Sierra Nevada Mountains can further swell the Sacramento and San Joaquin rivers. Peak flows from the local watersheds are generated shortly following storm events, since the local snow pack is typically non-existent.

Seasonal variations in freshwater inflow largely determine dissolved selenium loads delivered to the Bay. Wind and tidal forcing influence the mixing of water in the Bay and the dilution of dissolved selenium. Particulate selenium associated with sediments can be influenced both by flow and in-situ resuspension (driven by wind and tidal forcing). During the high flow season, hydrological forcing is probably more important as residence time in the Bay is short. During low flow, tidal and wind forcing play a more important role in mixing of water and the resuspension and redistribution of sediment associated selenium.

2.4. CONCEPTUALIZATION OF SEDIMENT TRANSPORT

The overall process of sediment cycling is referred to as the sediment budget and is shown in Figure 2-3. The sources of sediments include:

- Runoff, including erosion, from urban and nonurban sources within the watershed as well as input from the Delta, as shown in the upper left-hand portion of Figure 2-3. These loads are highly variable from year to year, and from the dry season to the wet season, as illustrated by the conceptual sediment loading rate inset to Figure 2-3. During the dry season, less sediments are transported in those streams due to lower stream flow velocities and low stream energy available to transport the sediments.
- Point sources. In contrast to the large seasonal and yearly variability of loadings from nonpoint sources, point source loadings are more constant temporally. Point source loadings of solids are small compared to nonpoint source loadings. During the dry season, point source loadings can exceed nonpoint source loadings.
- Exchange of suspended solids with Bay waters from outside of the study area, as well as exchange with bedded sediments through bed load transport.
- In situ particle generation (e.g., growth of phytoplankton) and particle depletion (e.g., consumption or death and decay of phytoplankton).
- Erosion from and deposition to the sediment bed.

Studies on sediment erosion and deposition done by the USGS (http://sfbay.wr.usgs.gov/sediment/suisunbay/results.html and http://sfbay.wr.usgs.gov/sediments/sanpablobay/intro.html) have shown that both Suisun Bay and San Pablo Bay have been net erosional regions over a number of years and appear to be contributing about 290 kg-Se/yr to the water column in the NSFB, as discussed in more detail in TM-2.

Solids that enter NSFB from freshwater inflows are subject to flocculation, since the salinity of the bay is typically high enough to destabilize the solid particles (salinities typically range from 5 to 35 psu). Once in the Bay, the solids are also subjected to gravitational forces and depositional shear stresses that tend to cause them to settle to the bed, as well as hydrodynamic forces such as erosional shear stresses that tend to keep the solids suspended (McDonald and Cheng, 1996). Typically, the concentration profile of suspended solids with respect to depth is not uniform, and concentrations increase with depth.

Within the water column, the solids are likely to consist primarily of the smaller clay-sized particles. In the bed, larger-sized particles are likely to be present, as well. A conceptualization of the particle size distributions is included in Figure 2-3. Particle size distributions are likely to vary temporally, from season to season, as the sources of those particles (and the forcing functions that influence their fate) change (Thompson-Becker and Luoma, 1985). Because of the many processes and the time scales associated with their manifestation, the accurate quantification of sediment resuspension, transport, and deposition is difficult (McDonald and Cheng, 1996).

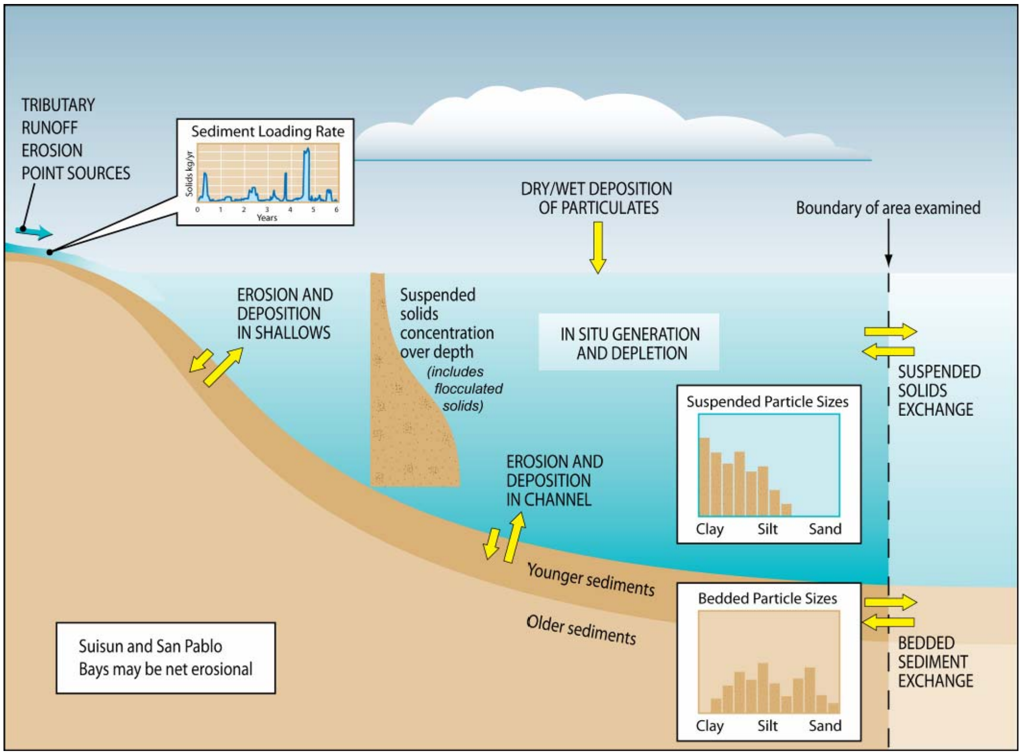


Figure 2-3 Conceptualization of Sediment Budget for NSFB

Continuous monitoring in the Bay by the USGS suggests that suspended sediment concentrations (SSC) are highly variable, and are driven by spring tides, wind, and freshwater flow. SSC concentrations measured in Honker Bay correspond well with the freshwater discharge from Delta. During the spring and summer months, wind-wave resuspension controls SSC concentrations in shallow channels.

2.5. Selenium Uptake by Bacteria and Phytoplankton

In oxic water columns, as in the NSFB, selenite and, to a lesser degree, selenate, can be taken up directly by phytoplankton and bacteria. Selenium exists in reduced organic forms within algal or bacterial cells or is exuded as dissolved organic selenium. Organic selenium in algal cells is highly bioavailable to organisms that consume them, such as zooplankton and bivalves (Luoma et al., 1992; Schlekat et al., 2000). Accurate estimation of bacterial and planktonic selenium is therefore key to assessing bioaccumulation. An understanding of the basic processes is especially important to predict what might happen if conditions were to change in the future, perhaps with decreasing selenium levels in the water column, or changing abundance of algae.

Algal selenium uptake varies widely across species. Studies on various types of marine algae by Baines and Fisher (2001) have shown that, for the same ambient concentrations, selenium concentrations in algal cells vary by 4-5 orders of magnitude depending on the species being considered. Chlorophytes typically exhibited the least enrichment, and dinoflagellates exhibited the greatest enrichment. Similar results of variable algal uptake of selenium were also reported in laboratory incubations by Doblin et al. (2006). The mechanistic causes underlying these inter-specific differences are not known. These data suggest that variations in algal communities over time may be partly responsible for changes in particulate selenium concentration. Particulate data on selenium is not collected to resolve this level of differences and these factors are indicative of significant uncertainty in predicting concentrations of selenium in bacteria and algae.

Laboratory tests over concentration ranges of interest in NSFB have also demonstrated that algal uptake of selenium may change in a non-linear manner in response to water column concentrations. Saturation, or near saturation, in cellular selenium concentrations is reached at low ambient selenium concentrations. In tests conducted with selenite, the most bioavailable form of selenium, several marine phytoplankton species examined by Baines and Fisher (2001) showed less than 2-3 fold change in cellular selenium concentrations, even with a 30-fold change in water column concentrations (0.15 nM versus 4.5 nM; Figure 2-4). These results contradict prior findings on freshwater species by Riedel et al. (1991) and Reidel et al. (1996) which might have been confounded by abiotic selenium uptake by dead algal cells. The Baines and Fisher (2001) results suggest that the uptake of selenium is not passive, but rather an enzymatically mediated process, with cells adjusting their intake depending on ambient concentrations. These authors suggest that over the range of selenite concentrations in NSFB, small changes in algal selenium concentrations are expected (65% change in cellular selenium concentrations for ten-fold range of water column concentrations from 0.1-1 nM; Figure 2-5).

The general findings of the Baines and Fisher (2001) work are very relevant to the TMDL: these laboratory tests indicate that algal selenium concentrations will stay nearly the same even when there are significant reductions in water column concentrations. Another way of thinking about this is to state that the bioconcentration factors are not constant over selenium concentration, but rather increase as selenium concentrations decrease. Although there are no data specific to NSFB that demonstrate this occurring, general literature reviews of bioconcentration factors across freshwater systems demonstrate that the highest ratios are observed at the lowest selenium concentrations (EPA, 2004; EPRI, 2006). Algal concentrations, in turn, affect the selenium concentrations in filter feeders, which may also respond weakly to changes in water column concentrations. This finding illustrates the potential limits of controlling bioaccumulation by reducing water column concentrations of selenium.

Planktonic uptake of selenium is further complicated by the fact that phytoplankton abundance is highly dynamic across seasons (Alpine and Cloern, 1992; Cloern et al., 2006; USGS water quality cruise data in the bay). Inter-annual plankton trends (as measured using chlorophyll a concentrations) have also exhibited interesting trends in recent years (Cloern et al., 2006; Cloern et al., 2007). During the late 1990s phytoplankton abundance was low, hypothesized to be due to increased grazing by rapidly increasing populations of the invasive Asian clam, *Potamocorbula amurensis*. However, more recently phytoplankton abundance has actually increased to levels of 30-40 µg/l of chlorophyll as seen in the early 1970s and 1980s prior to the *P. amurensis* invasion (Hogue et al., 2001). It is thought that these increases in phytoplankton abundance have been caused by suppression of grazing, which in turn is related to increased populations of organisms that prey on the bivalves (Bay shrimp, English sole, and Dungeness crab). This increase in predators is hypothesized to be related to cooler ocean temperatures, and increased migration into the bay (Cloern et al., 2007). Because of the significance of phytoplankton and bivalves in controlling the bioaccumulation of selenium, dramatic shifts in their relative abundances may have an impact on selenium concentration in other trophic levels.

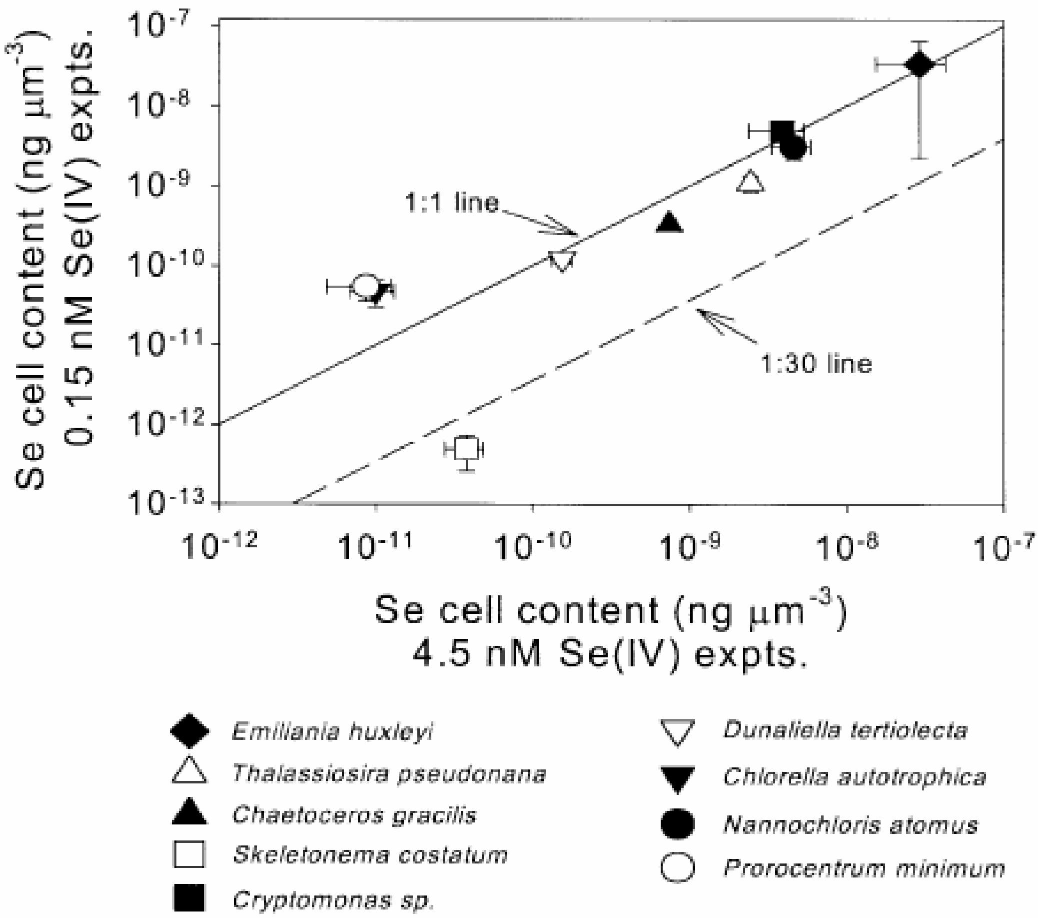


Figure 2-4 Comparison of algal selenium concentrations for nine species of algae grown at 4.5 and 0.15 nM selenite. The solid line represents the situation where cellular selenium concentrations are constant and independent of ambient selenite concentrations. The dashed line represents the case where cellular selenium concentrations vary in linear proportion to ambient selenite concentration. For cellular uptake at two concentrations, a thirty fold difference in ambient concentrations made practically no difference to the cellular algal concentrations. (Source: Baines and Fisher, 2001)

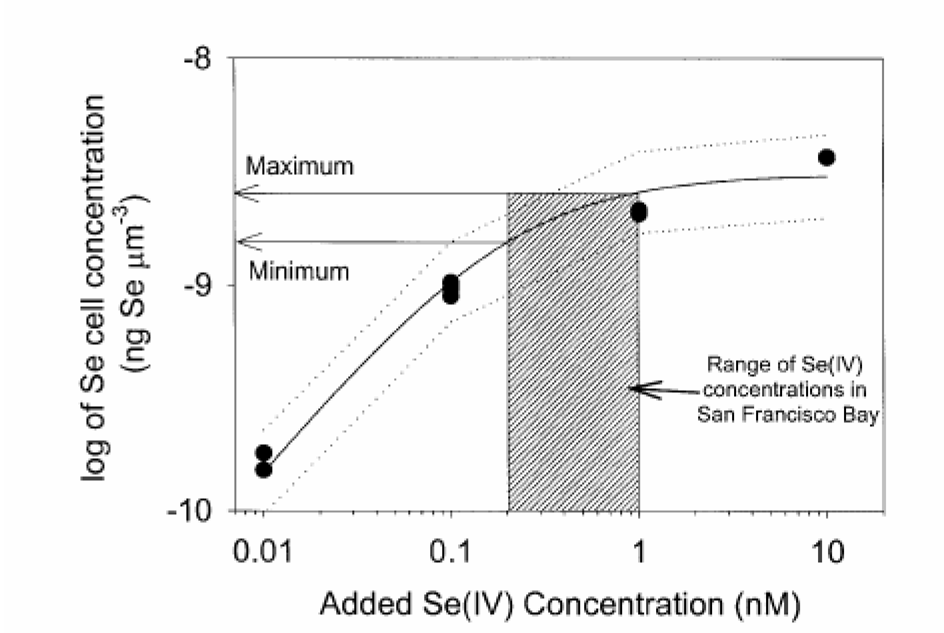


Figure 2-5 Relationship between Thalassiosira pseudonana cellular selenium concentration and external selenite concentration in controlled experiments. The line represents a best fit to the data. The shaded area indicates the range of selenite concentrations observed historically in NSFB. For this species, typical of the group shown in Figure 2-4, the change in cellular selenium is not linear with respect to changes in added selenite concentration.

2.6. SELENIUM UPTAKE BY ZOOPLANKTON AND BIVALVES

The uptake of trace elements at steady state, such as selenium, has been shown to be represented by an equation of the following form (Reinfelder et al., 1998; Luoma and Rainbow, 2005; Presser and Luoma, 2006):

$$C_{m,ss} = (I_f + I_w)/(k_e + g) \qquad \text{Equation 2.1}$$

Where,

$C_{m,ss}$ = Steady-state Se concentration in tissue, µg/g
I_f = Se influx from food
I_w = Se influx from water
k_e = rate constant for Se loss from organism, day^{-1}
g = rate of growth of organism
I_f = $(FR)(C_f)(AE)$
FR = feeding rate per gram of tissue, g-food/g-tissue/day
C_f = concentration of Se in food (concentration in particulate matter), µg/g
AE = assimilative efficiency of selenium in food consumed (depends on Se speciation) or fraction of ingested selenium taken up into tissues, g-assimilated/g-intake

Thus, accurate characterization of tissue concentrations in bivalves or zooplankton requires the quantification of a handful of parameters including the uptake from water, feeding rate, concentrations in food, and assimilative efficiency. Many of these parameters have been estimated through experiments for different chemicals and species (Luoma and Rainbow,

2005) and can be used to predict tissue concentrations, at least to an order of magnitude. Parameters for many species of interest in NSFB have been quantified.

Experimental studies in filter feeding organisms have shown that direct selenium uptake in the dissolved phase from water is minimal and, for most practical purposes, can be ignored (Luoma et al., 1992; Stewart et al., 2004). The direct uptake from water can be a larger source of selenium to zooplankton than bivalves (Stewart et al., 2004), although even for zooplankton, particulate selenium is a more important pathway than dissolved selenium. As shown in Figure 2-1, the bioaccumulation of selenium in bivalves occurs through particulates, whether planktonic or mineral in origin, and is only indirectly related to the dissolved phase concentrations. Dissolved selenium, if not converted to particulate form through biotic and abiotic reactions, is largely unavailable to bivalves.

Feeding rates and selenium loss rates from organisms have been estimated for key species of interest in NSFB, including the native clam, *Macoma balthica*, as well as the invasive species *P. amurensis*. High feeding rates and/or slow loss rates are likely to result in higher tissue selenium concentrations. In NSFB, *P. amurensis* has a feeding rate significantly higher than the native species, increasing the potential bioaccumulation (Lee et al., 2006). The selenium loss rate may also differ from organism to organism, and result in higher or lower bioaccumulation.

The assimilative efficiency is another important variable in determining bioaccumulation of selenium and has been shown to be strongly dependent on the chemical form of the particulate selenium. Selenium present in algal tissue is the most bioavailable form, whereas elemental particulate selenium is the least bioavailable (Luoma et al., 1992; Schlekat et al., 2000). In addition, it has also been found that the assimilation of selenium into bivalves from algae is dependent on the species of bivalve and the species of algae present (Schlekat et al., 2002).

2.7. SELENIUM UPTAKE BY HIGHER TROPHIC ORGANISMS

Selenium in benthic organisms can bioaccumulate to high levels in species that are dependent on the benthos for most of their dietary needs. In NSFB, the primary organisms that fit this category are benthic-feeding fish, such as the white sturgeon (*Acipenser transmontanus*) and diving ducks (Lesser scaup, *Aythya affinis*; Greater scaup, *Aythya marila*; Surf scoter, *Melanitta perspicillata*).

Organisms that feed on zooplankton, such as the striped bass (*Morone saxatilis*) may also be exposed to selenium, but data in the region do not suggest elevated concentrations in response to higher water column concentrations. For example, muscle tissue concentrations in striped bass at an upstream location in the Sacramento River (Clarksburg), where water column concentrations are very low and considered to be background (fish 0.42-0.46 µg/g dry weight over 1987-1990, water ~0.06 µg/l), were similar to concentrations measured near Antioch in the Delta, and in the bay, where higher water column concentrations occur (fish 0.39-0.44 µg/g dry weight over 1986-1990, water ~0.4 µg/l) (sampling performed as part of the Selenium Verification Study, Urquhart et al., 1991). Further, the levels were similar to those observed in a nationwide survey, and are thought to be background concentrations.

In most instances the bioaccumulation process is represented through simple linear relationships between diet concentrations and concentrations in tissues of higher trophic organisms. Data and correlations are typically reported for muscle tissue and for livers, an organ where selenium has a propensity to concentrate to very high levels. For comparison of data across space or time, it is vital to ensure that the same tissue-type is being considered. A list of correlations for species pertinent to NSFB (Greater and Lesser scaup and White sturgeon) with concentrations in different species of bivalves has been summarized from the primary literature by Presser and Luoma (2006). The squares of the correlation coefficients (r^2) show values of 0.6 or greater and significant positive slopes, indicating significant elevation of concentration from bivalve to predator. Selected relationships are illustrated graphically in Figure 2-6. The best-fit lines in these plots are most useful to illustrate a general relationship: specific data points sometimes pair data from different years. The nature of the relationship at the high end of the x-axis values also leaves room for uncertainty: It appears that the highest concentrations in bivalves (represented by *P. amurensis* data) do not result in a corresponding increase in tissue concentrations. However, this interpretation is complicated by the fact that the tissue concentrations in birds in the original reference were from several years prior to when the *P. amurensis* concentrations were measured.

Higher trophic level predator concentrations can also be examined in conjunction with the framework used for zooplankton and bivalves in Section 2.6 (this equation was implemented as a model, DYMBAM by Presser and Luoma, 2006). The predicted concentrations are shown for a range of assimilative efficiencies for bivalves, and using regressions between bivalve concentration and higher trophic organism tissue concentration (Figure 2-7). The plots show the wide range of bivalve concentrations that may result from similar particulate selenium concentrations, with different assumptions of selenium assimilative efficiency, given a set food intake rate and selenium loss rate. The different values of assimilative efficiency correspond approximately to the range observed using different forms of particulate selenium for feeding bivalves in laboratory studies (elemental selenium is least available, and algal selenium is most available). The following values were used in Equation 2.1 to create Figure 2-6-7:

k_e = 0.02 day^{-1}
FR = 0.2 g-food/g-tissue/day
AE = 0.5 or 0.8 (dimensionless)

Estimates of predator concentrations were made using the best-fit linear regressions shown in Figure 2-6. Concentrations are shown to vary over a wide range, especially for scoters. Even when the particulate concentrations vary over a fairly narrow range, typically 0.5 to 2 μg/g, the resulting tissue concentrations in scoters are estimated to range between 10 and more than 70 μg/g. The wide range of possible tissue concentrations estimated through this simple predictive framework highlights the need for obtaining site specific data where the dietary concentrations are related to tissue concentrations. Note that higher trophic level tissue concentrations are not based on the DYMBAM formulation but rather on direct regressions with bivalve concentrations. Direct laboratory experiments to determine assimilative efficiency and other parameters in Equation 2.1 have not been performed for higher trophic level species of interest in NSFB. Such experiments are considerably more complex to perform for larger, mobile species, and the lack of such direct diet-tissue relationships is a source of uncertainty.

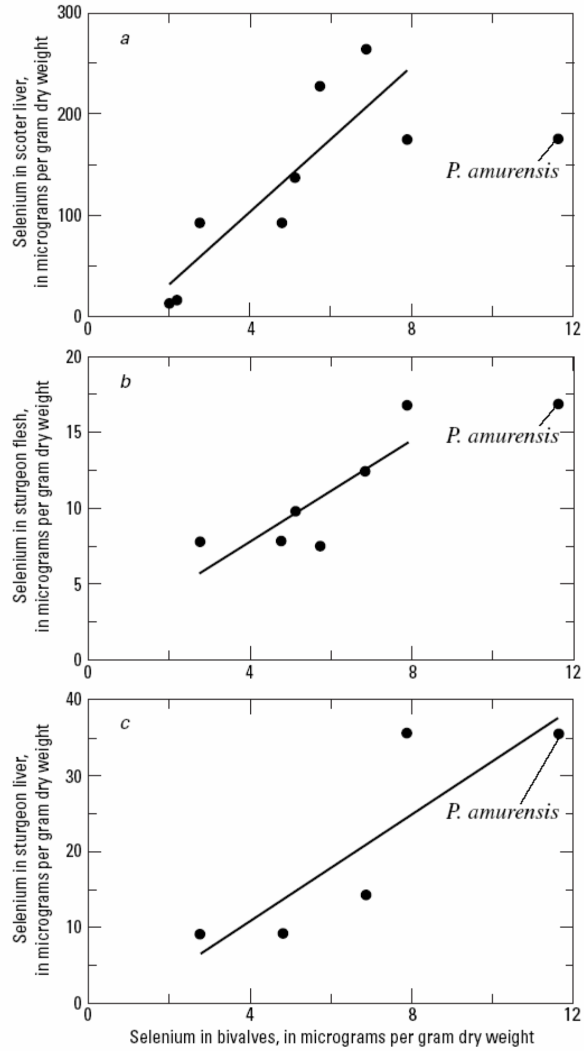


Figure 2-6 Relationship between prey and predator concentrations (reproduced from Presser and Luoma, 2006, based on source data from the late 1980's Selenium Verification Study, White et al., 1987, 1988, 1989). The prey are the bivalve *Corbicula fluminea*, except for some data points, where they are for *P. amurensis.* The latter species is identified separately because it has been associated with comparatively higher selenium tissue concentrations.

2.8. SUMMARY OF SELENIUM BEHAVIOR IN NSFB

Selenium cycling and biological uptake has been studied extensively in NSFB, and the principal mechanisms are well known. The main features of selenium behavior in the water column, sediments, and biota are summarized below.

2.8.1 Water column

Selenium enters NSFB in dissolved and particulate forms from the Delta, from point sources such as the refineries and municipal wastewater treatment plants, and from local tributaries. Both dissolved and particulate selenium can exist as different species that affect their cycling and bioavailability. Dissolved selenium can be taken up and bioconcentrated by algae and bacteria in the water column and add to the supply of particulate selenium. Selenite is the most bioavailable and bioaccumulative form of dissolved selenium. The exchange between selenate and selenite is slow, and is unlikely to occur significantly over the residence times in the bay. Conversion of selenite to organic selenide forms through microbial uptake is more rapid and is likely to be important in the bay.

2.8.2 Sediments

Depending on the flow rate and season, deposition to and erosion from the sediment bed can also be a sink/source of particulate selenium to the water column. Sediments are more reducing than the water column, and may result in conditions that reduce selenate and selenite to elemental selenium, Se (0), a form that is insoluble and less bioaccumulative than selenite.

2.8.3 Biota

Because of the preferential partitioning of some forms of selenium onto particles (both organic and inorganic), they are a comparatively rich source of selenium to organisms that consume them. Filter-feeding benthic organisms such as bivalves ingest and assimilate the particulate forms of selenium at different efficiencies depending on the type of particulate material. Direct ingestion of dissolved selenium is minimal for organisms besides plankton and bacteria. Bivalves typically biomagnify selenium to concentrations higher than found in the particulate phase. When these organisms are consumed by predator species such as sturgeon and diving ducks, the selenium is biomagnified further in the tissues of these animals. Algal and bacterial-associated selenium can also enter the food through a non-benthic pathway, i.e., through zooplankton that feed on these organisms, and through consumer organisms that feed on zooplankton.

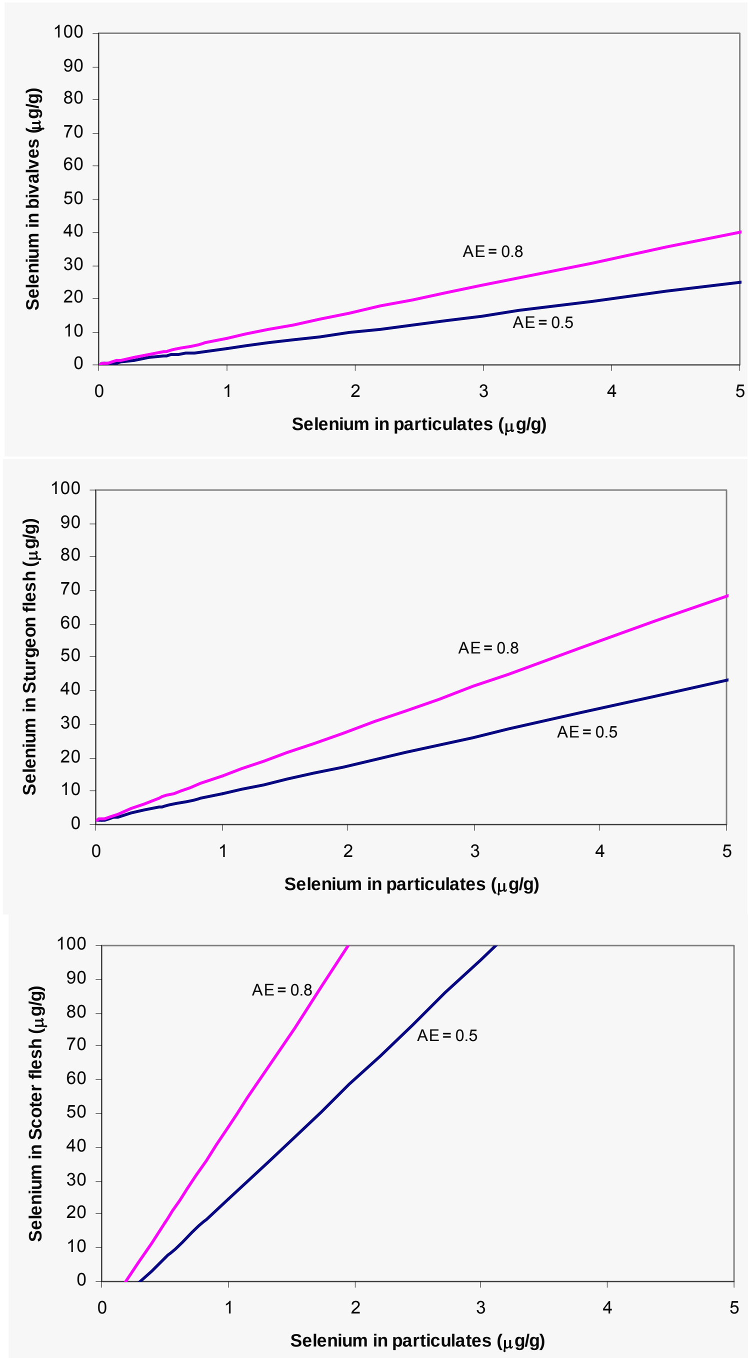


Figure 2-7 Relationship between selenium in particulates consumed by bivalves (top panel), and concentration in flesh of predators that consume those bivalves, lower two panels for sturgeon and scoter. The calculations assume two values of assimilative efficiency (AE, of 0.2 and 0.8) for selenium in bivalves. The bioaccumulation to higher trophic levels employs the regressions shown in Figure 2-6 (from Presser and Luoma, 2006).

3. Recent Selenium Data from NSFB

The prior section summarized research knowledge of selenium cycling and uptake, with an emphasis on conditions and species that occur in NSFB. This section presents a more detailed review of selenium concentration data in different environmental media from recent and ongoing monitoring programs.

Because of the vast amount of work performed on selenium cycling in the NSFB, and the existence of excellent reviews summarizing historical data (principally Presser and Luoma, 2006), this analysis is focused on more recent data (in the 1990s and beyond) that are more closely related to future actions as part of the selenium TMDL. The focus on recent data also acknowledges that present-day loading conditions are different from historical conditions, especially for the point sources associated with refineries. In addition, there have been reductions in concentrations from the San Joaquin River in recent years, which may continue to trend downward in the future.

Data on selenium in the following forms is discussed below: dissolved, particulate, sediment, algal and bacterial, in prey items, and in predator species such as fish and diving ducks. This section also presents a review of bioconcentration and bioaccumulation factors for selenium in the bay.

3.1. Dissolved Selenium

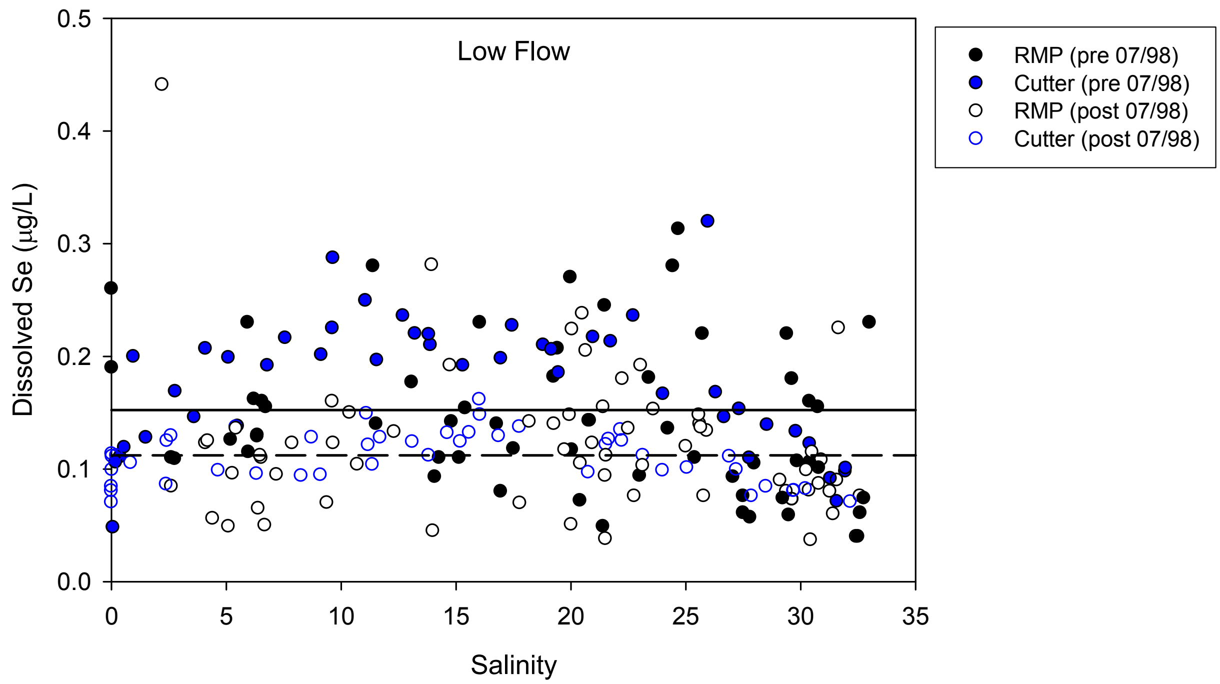
Table 3-1 summarizes speciation data for NSFB, cores, pore water, refineries, and wastewater treatment plants. Dates are provided to indicate when the data were collected. In refinery effluents, the fraction of selenium discharged as Se +IV dramatically decreased (from 65% to 13%), following improved wastewater treatment in 1998. At the other extreme, in the San Joaquin River, only 3-5% of the dissolved selenium is Se +IV. Selenate (Se+VI) is the dominant form in the bay waters, San Joaquin River, and in municipal discharges and current refinery discharges. Organic selenium is a significant component of most sources, and may be generated naturally through biological reduction processes occurring in the rivers, the Delta, and in the bay.

Aside from non-point source load changes caused by hydrologic variability, the refinery load reductions in 1998 have been the largest change in selenium loads in the recent history of the bay, and especially so in the dry season. Figure 3-1 shows changes in dissolved concentrations before and after refinery cleanup. Wet season and dry season concentrations, on average, show declines in the mid estuary regions where the refineries discharge. However, there is considerable scatter and spatial variability, and there is overlap in the concentration ranges associated with pre-refinery cleanup years and post-refinery cleanup years.

Figure 3-2 summarizes how various species of selenium within the North Bay have changed in selected sampling events between 1986 and 1999. For the most bioavailable form of selenium (selenite, Se+IV), relative concentrations in the North Bay have clearly decreased. The Se +IV concentration as a percent of total dissolved selenium is plotted in Figure 3-3 for high flow conditions (panel a) and low flow conditions (panel b). The most distinguishing feature of the plots is that the fraction of dissolved selenium present as Se +IV has significantly diminished over time (from 25-40 percent to 10-15 percent).

Table 3-1
Qualitative Description of Selenium Speciation

Category	Description
Bay Waters (Similar to speciation used by Meseck and Cutter, 2006)	Low flow, dissolved selenium: • Se+VI: 50-60% • Se+IV: 20% • Se-II: 20%-30% High flow, dissolved selenium: • Se+VI: 40-50% • Se+IV: 30-40% • Se-II: 10-30%
Total Selenium in Sediment Cores (Meseck, 2002, late 1990's data)	• Se (0): 60% • Se+VI plus Se+IV: 15-20% • Se-II: 20-25%
Pore Water (Meseck, 2002, late 1990's data)	• Se+VI plus Se+IV: 60-80% Near surface; depletes with depth • Se-II: mirror image
San Joaquin River (1999 – 2000)	Dissolved • Se+VI: 60-70% • Se+IV: 3-5% • Se-II: 25-35%
Refineries: 1980s and 1990s	In 1980s: • Se+IV: 64% Subsequent to late 1990s: • Se+VI: 57% • Se+IV: 13% • Se-II: 30%
Non-refinery point source discharges, primarily municipal wastewater (1989 – present)	• Se+VI: 60% • Se+IV: 25% • Se-Ii: 15%



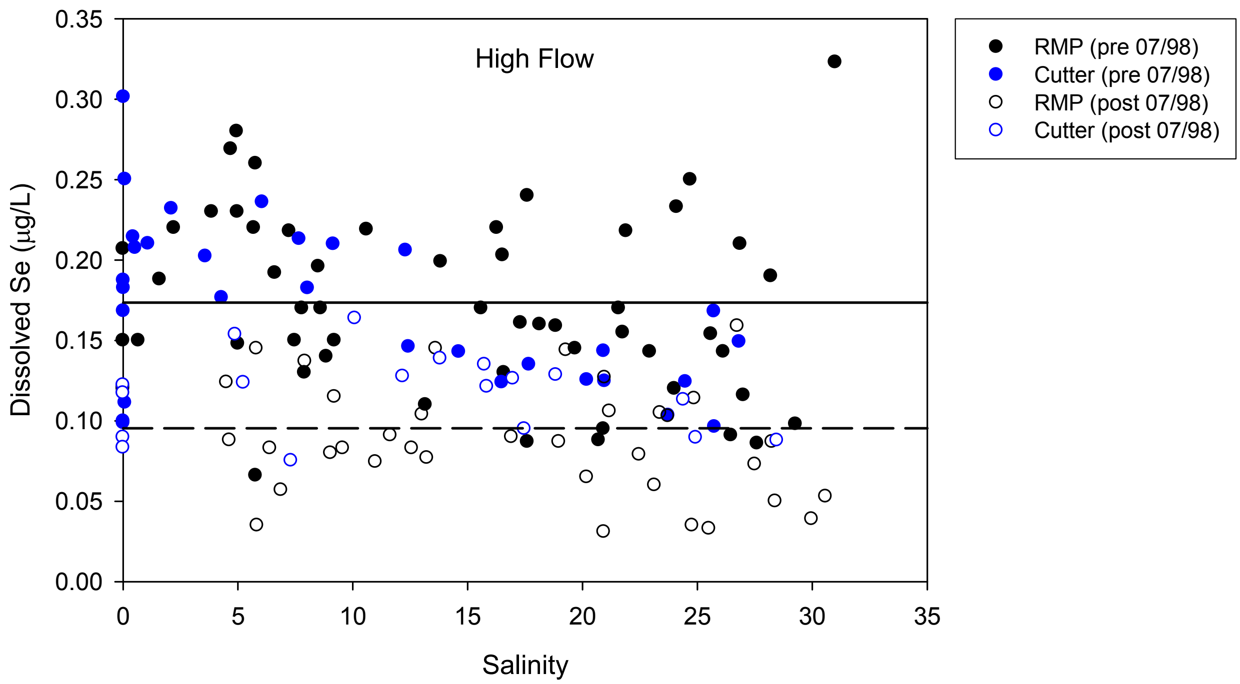


Figure 3-1 Dissolved selenium concentrations under low and high flow before and after July 1998 (data: RMP and Cutter and Cutter, 2004). The July 1998 cutoff date represents samples before and after improved wastewater treatment at the North Bay refineries. Overall mean for pre 07/98 (solid line) and post 07/98 (dashed line) are also shown.

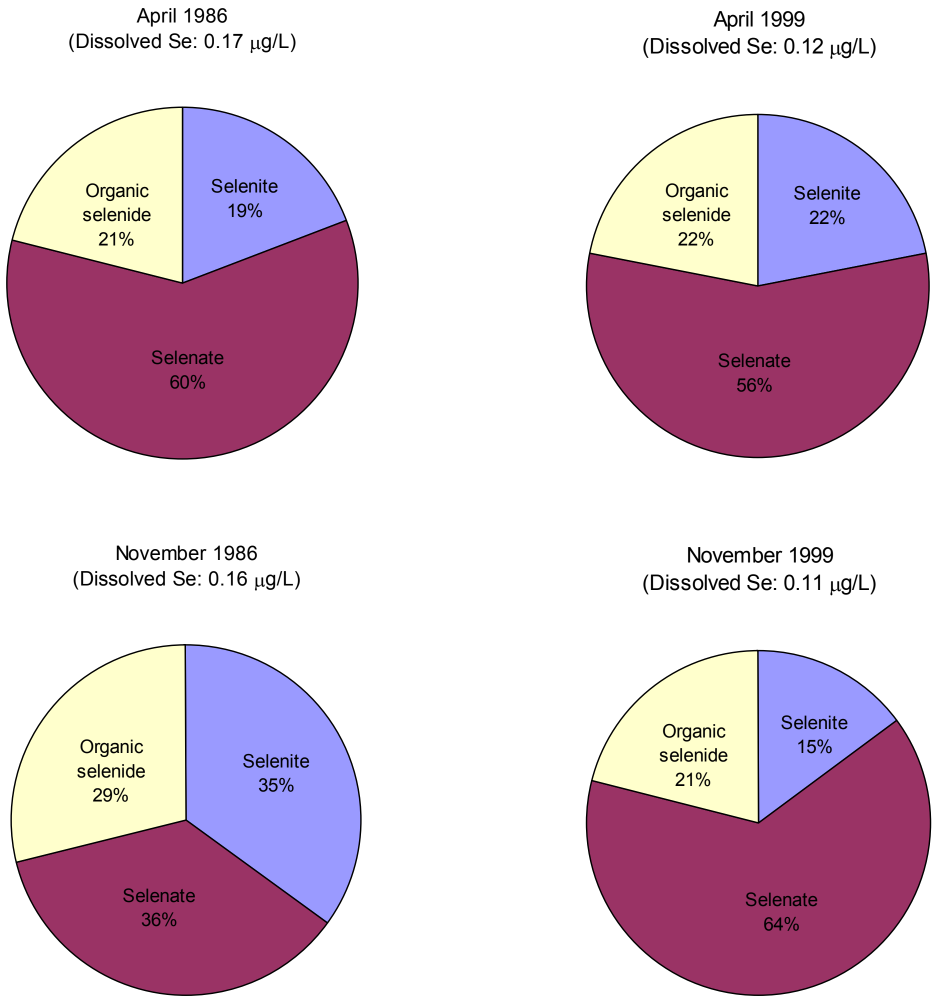
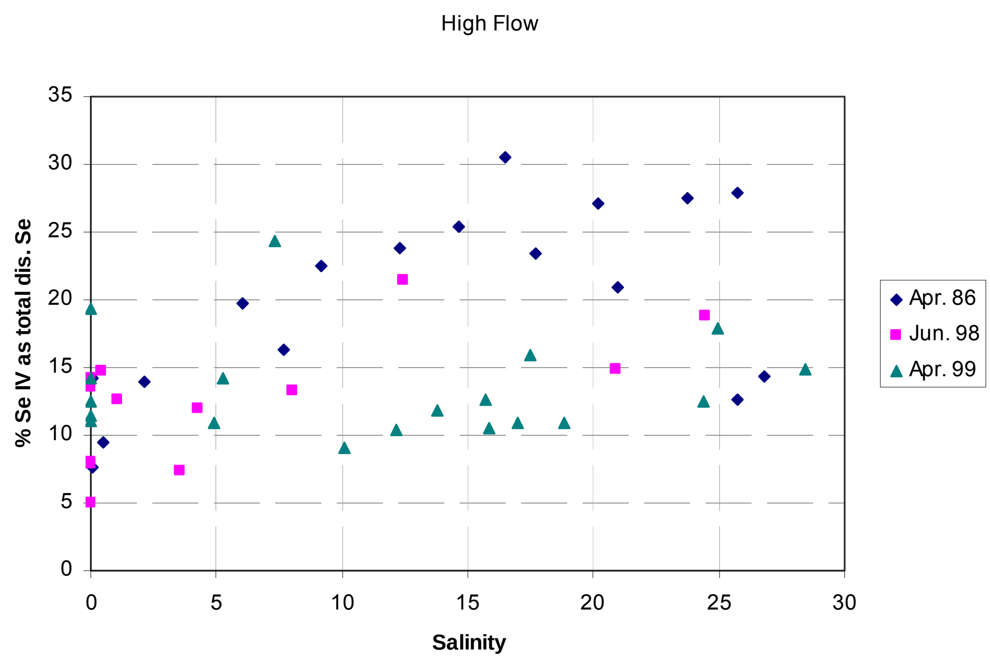


Figure 3-2 Speciation of dissolved selenium in the bay water column during different time periods (Data: Cutter and Cutter, 2004).

(a) High Flow



(b) Low Flow

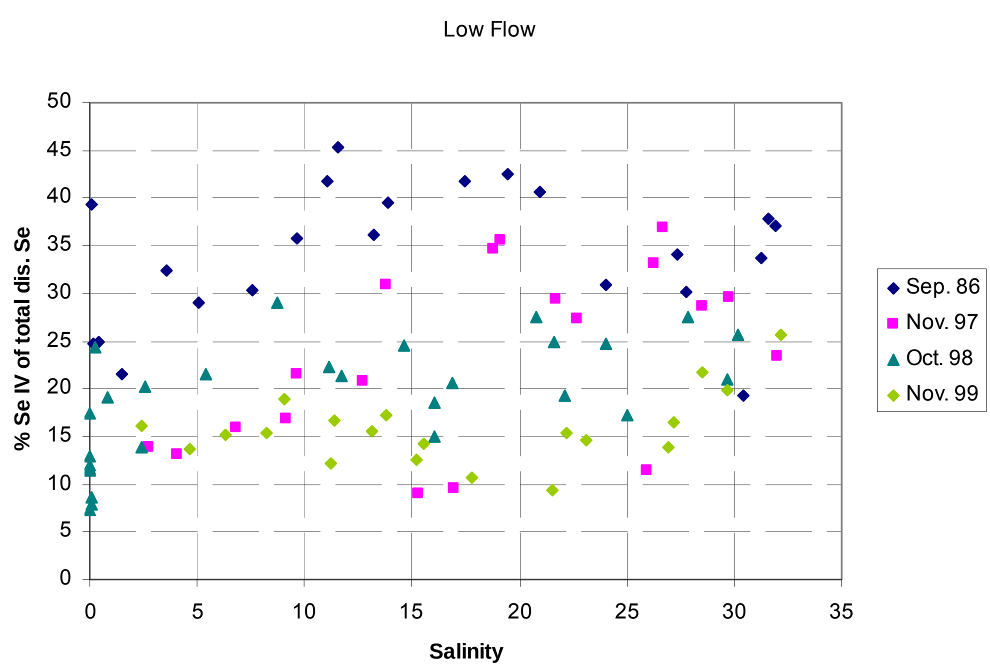


Figure 3-3 Se +IV percentage for four sample periods, during high flow and low flow conditions.

3.2. Particulate Selenium in the Water Column

Although most selenium in the water column at any given time is in one of the dissolved forms, the relatively small fraction (2-18.5%) that is particulate is far more available to bivalves and zooplankton, and is therefore of special significance from the standpoint of bioaccumulation. This section presents a detailed overview of the sources, distribution, speciation, and partitioning of selenium on particulates, largely based on the work of Doblin et al. (2006).

3.2.1 Sources of Particulate Selenium

Suspended materials in NSFB waters include mineral particles, particulate organic matter (non-living) and living organic matters (primarily algae and bacteria). These particulate sources may originate from the various non-point sources to the bay, as identified in TM-2, may be generated in situ, or may be eroded from the sediment bed. Point sources are a relatively small source of particulate loads. Selenium is associated with each of the particulate forms, either sorbed on mineral or non-living particulate organic matter, or associated with the bulk material of the particles when taken up by algae/bacteria or eroded as elemental selenium particles.

In general, particulate elemental selenium is associated with bed sediments, and particulate organic selenium is associated with algal/bacterial uptake, and selenite and selenate are associated with sorption to mineral particles and/or particulate organic matter. Although a simplification, these relative sources can be used to compare spatial and temporal trends in the plots that follow.

3.2.2 Distribution of Particulate Selenium

Doblin et al. (2006) reported the variation of total suspended particulate material (TSM), and selenium on particles in San Francisco Bay in 1997-1999. Particulate selenium content, including speciation, was measured directly using material collected on 0.4 µm filters. Particulate selenium was reported as the mass of selenium per unit volume of water or as the mass of selenium per unit mass of particles. The latter measure normalizes for the effect of changing TSM in water samples at different locations and times.

Selenium concentrations in the particulate phase of the water sample (µg/l), or expressed as the concentration on suspended solids (µg/g), although variable across location, do not show a consistent temporal trend, as noted in sampling in the 1980s and late 1990s (Figure 3-4). Higher selenium contents on particles were observed under low flow conditions (Table 3-2) for both time periods.

Particulate selenium concentrations along the salinity gradient generally track the pattern in TSM, and decrease along the salinity gradient during high flow (Figure 3-4). Selenium concentrations in particulate material are generally lower during high flow than low flow (Doblin et al. 2006), although some high values (including one as high as 1.6 µg/g) were measured in the bay. For the sampling periods shown in Figure 3-4, chlorophyll a concentrations were low in all years except 1986. However, as discussed earlier, this trend may be reversing in more recent time periods, although there are no accompanying selenium data.

During low flow, TSM concentrations also decrease slightly with an increase in salinity (Figure 3-5). TSM concentrations show occasional increases in the middle of estuary, possibly due to resuspension. Particulate selenium concentrations track the patterns in TSM (Doblin et al. 2006), most evidently for the September 1986 and November 1999 transects. Selenium concentrations in particulate material exceed values measured during high flow and also show some increase with increase of salinity (up to 2.2 μg/g). For the October 1998 and November 1999 transects, chlorophyll-a concentrations are relatively constant throughout the bay with some increases in the Central Bay.

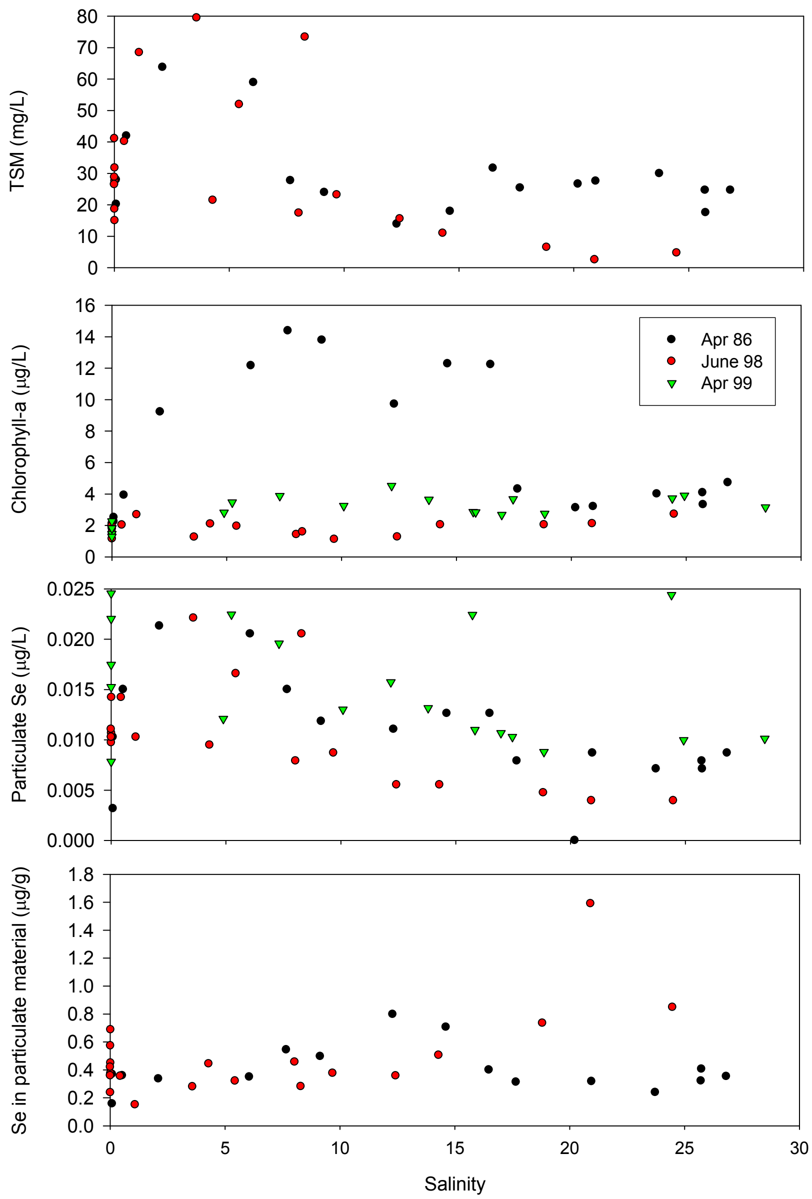


Figure 3-4 High flow: Transects of TSM, chlorophyll-a, particulate selenium and selenium in particulate material (April 1986, June 1998 and April 1999; Doblin et al. 2006 and electronic database provided by Dr. Cutter).

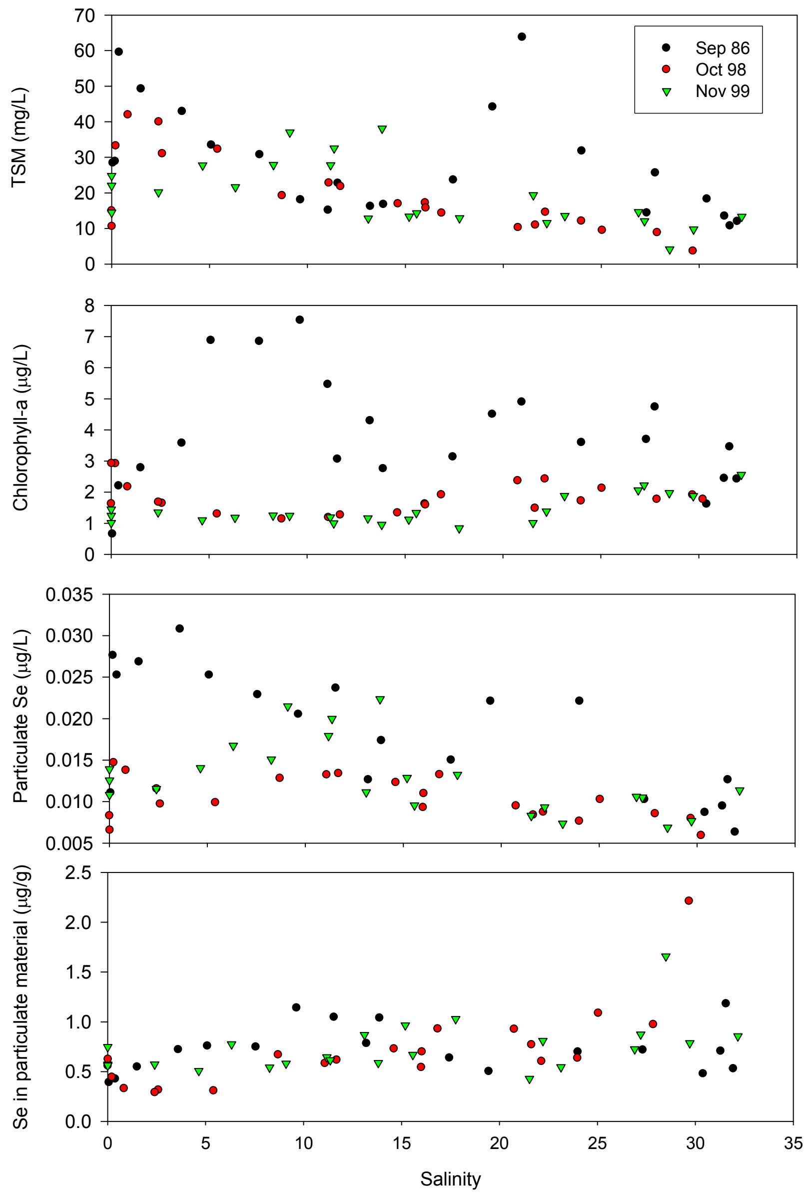


Figure 3-5 Low flow: Transects of TSM, chlorophyll-a, particulate selenium and selenium in particulate material (September 1986, October 1998, and November 1999; Doblin et al. 2006 and electronic database provided by Dr. Cutter).

Particulate selenium concentrations, expressed as µg/l, vary less over time than TSM (Table 3-2), although selenium content in suspended particles differs between low flow and high flow conditions. Low flow periods were found to have higher selenium content in suspended particles, most likely due to longer residence time and accumulation by phytoplankton and bacteria (Doblin et al. 2006).

Table 3-2
Summary of particulate concentrations during low and high flow periods (Doblin et al. 2006).

	Low Flow			High flow	
	Oct. 1998	**Nov. 1999**	**Nov. 1997**	**June 1998**	**April 1999**
TSM (mg/L)	19.1 ± 10.4	19.4 ± 8.8	13.1 ± 5.8	30.2 ± 22.0	31.2 ± 20.0
Particulate Se (μg/L)	0.010 ± 0.002	0.013 ± 0.004	0.010 ± 0.003	0.010 ± 0.005	0.015 ± 0.006
Se content in particulate (μg/g)	0.70 ± 0.41	0.73 ± 0.25	0.87 ± 0.30	0.49 ± 0.31	--
Se: C ratio (X 10^{-6})	4.7 ± 3.1	5.9 ± 2.7	6.5 ± 2.5	4.1 ± 2.0	3.0 ± 1.0

Particulate selenium concentrations are related to TSM with lower selenium concentrations at higher TSM levels (Figure 3-6). These data indicate that there is a minimum particulate selenium concentration in the system, perhaps from bed sediments, that dilute higher Se concentrations associated with plankton and organic matter. This is also shown in the higher percentage of carbon in TSM when TSM values are low (Figure 3-7). Higher suspended bed sediments, which may occur during low flow and high flow events, decrease the relative influence of the plankton and organic-associated selenium.

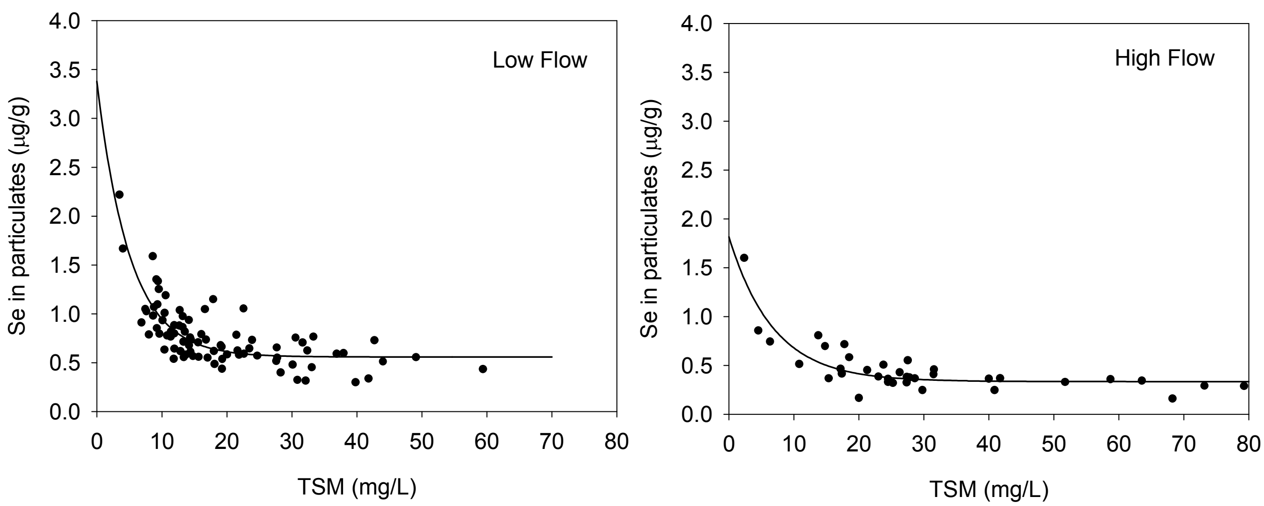


Figure 3-6 Selenium as a function of TSM under high flow and low flow conditions (all data between 1986 and 1999 in electronic database provided by Dr. Cutter).

The behavior of selenium on particles is complex, and exhibits the relative and time-varying contributions of different particle types, broadly classified as mineral and organic. Over the time period investigated, particulate selenium concentrations (computed as µg/g) do not show a temporal effect of the refinery point source load reductions, in manner seen for dissolved phases. Indeed, these concentrations, although variable, remain at about the same average levels across a long period of measurements from 1986 to 1999. These data will be key component of any modeling of selenium cycling that is done as part of the TMDL.

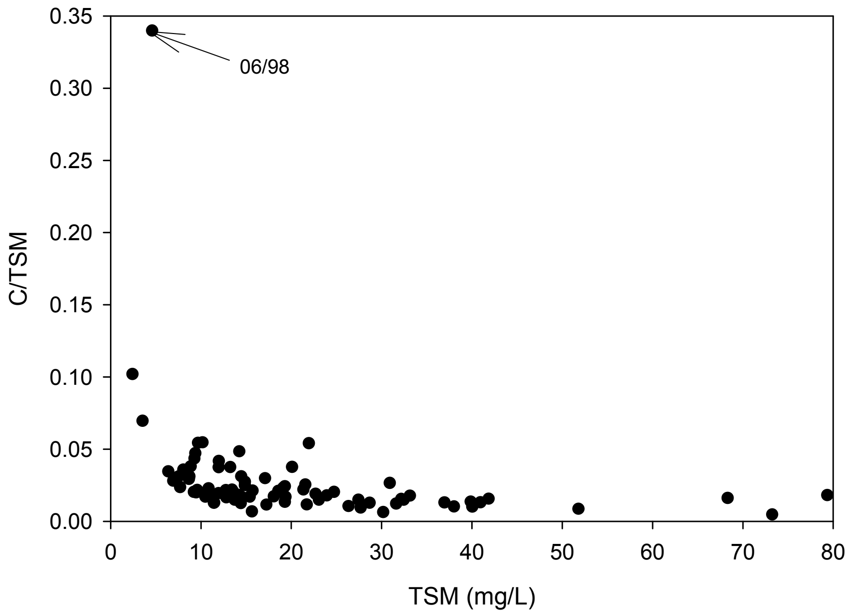


Figure 3-7 Ratio of particulate carbon to TSM over all sampling dates (all data between 1986 and 1999 in electronic database provided by Dr. Cutter).

3.2.3 Speciation of Selenium on Suspended Particles

Additional insight into the cycling and potential uptake of selenium by filter feeding organisms can be provided by data on the speciation of particulate selenium. Controlled experiments have shown the relative assimilative efficiency of different forms of particulate selenium. Organic selenium, especially when associated with living algae is most bioavailable, whereas elemental selenium is the least available to feeding bivalves.

Doblin et al. (2006) reported particulate selenium speciation data in 1997-1999 in the bay. Selenium species on particulate material were found to be dominated by organic selenide (45 ± 27%), followed by elemental selenium (35 ± 28%), and adsorbed selenite and selenate (20 ± 10%). The percentage of organic selenide is roughly similar during low and high flow periods. Speciation of particulate selenium is shown in Figure 3-8. Overall particulate concentrations show an increasing trend with salinity, largely due to higher organic selenium concentrations. The mix of forms appears is variable, although the data demonstrate the significance of the elemental selenium and organic selenium. Organic selenium levels increase with travel distance in the estuary, indicating that processes in the estuary are converting other forms of selenium (likely selenite) to organic forms, and that it is not merely being imported from upstream sources in the Delta.

These data can provide the calibration basis for a mechanistic model of selenium cycling and uptake that is being proposed for the selenium TMDL.

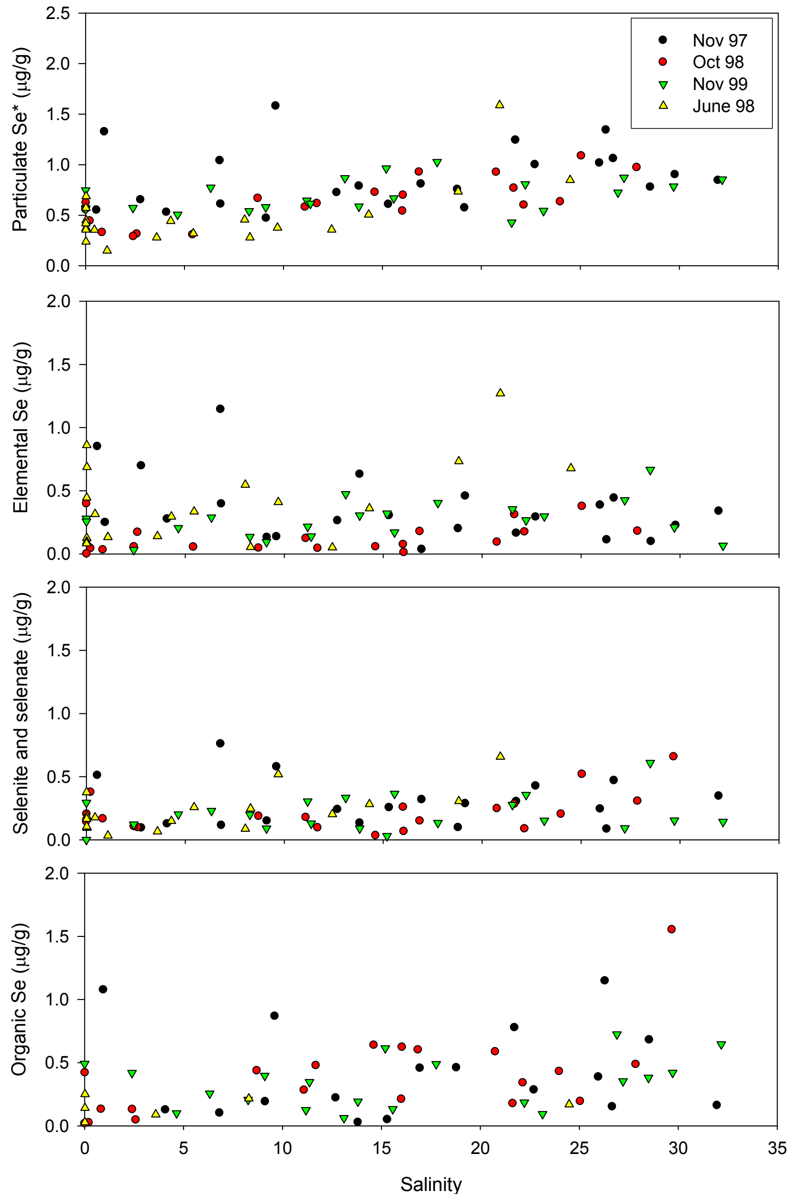


Figure 3-8 Transects of total particulate selenium, particulate elemental selenium, particulate adsorbed selenite and selenate, and particulate organic selenium (Doblin et al. 2006). (*Particulate Se includes all forms of selenium; organic Se is computed as the difference between particulate Se and inorganic forms).

3.3. SEDIMENTS

The sediment environment influences the speciation of selenium in ways that differ from the water column. A major difference between the water column and sediments is the fact that the oxidation-reduction potential is lower in the sediments. In the water column, dissolved oxygen is typically present at concentrations that support an oxidizing condition. Thus, selenium is likely to be present there in more oxidized forms (such as selenate and selenite). Oxidation-reduction conditions are likely to change and become more reducing with increasing depths into the sediments. The few sediment core samples (Meseck, 2002) analyzed for selenium support this; but they extend less than 15 cm.

Selenium concentrations in a reducing environment can be controlled by solubility. For example, selenium may precipitate as metal selenides or elemental selenium. Average selenium concentrations for sediment cores, 5-15 cm deep, collected by G. Cutter's research group range between 0.22-0.41 µg/g in the North Bay. Selenium in sediment cores is found to be dominated by elemental selenium (Meseck, 2002). Elemental selenium accounts for a median of 45% of the total selenium in the sediments across the sites, with selenite and selenate accounting for a median of 17%. The difference between total, elemental and selenite and selenate is the organic selenium. Selenium concentrations are generally uniform in the sediment cores, although some variations along the depth were observed (Cutter, unpublished data).

Living organisms on or within the sediments, such as polychaetes or bivalves, can bioturb the sediments, and provide preferential pathways for selenium to be diffused and advected back into the Bay waters, and at the same time alter the oxidation-reduction potential. Not only can organisms such as bivalves provide preferential pathways, but they can bioirrigate the sediments by pumping the water as they feed. Also, biomethylation of selenium in sediments can be important under moderately reducing conditions. The dissolved selenium in sediment pore water can exchange with the overlying waters or deeper sediments depending on the magnitude and direction of the concentration gradient. The few data available indicate that pore water dissolved selenium concentration is similar to dissolved concentrations in the water column, and thus diffusion rates are thought to be small.

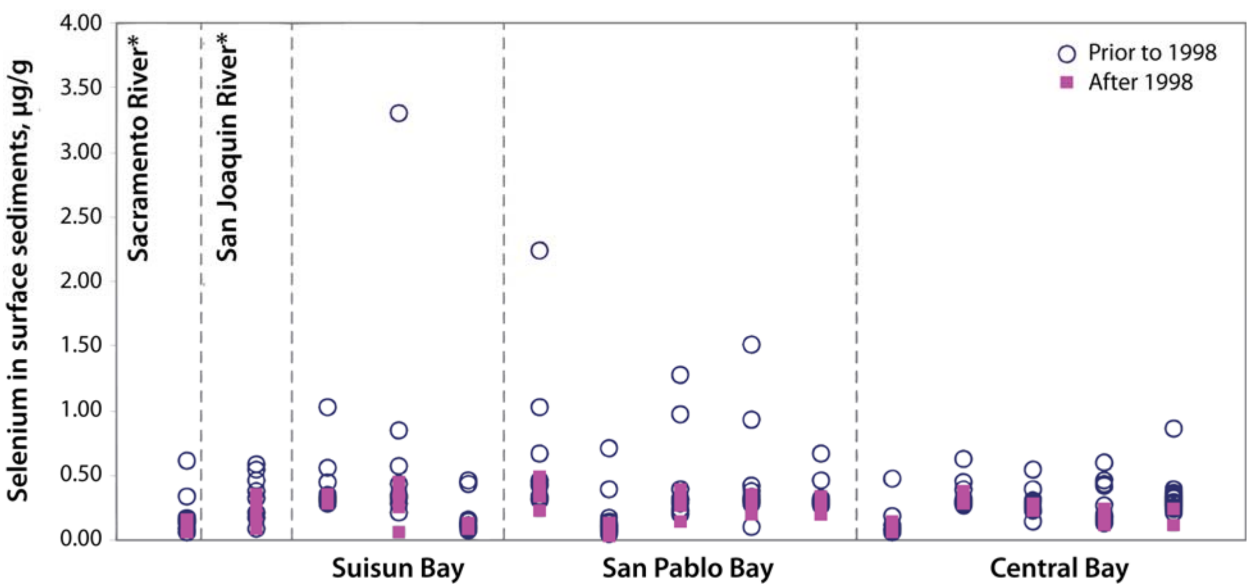


Figure 3-9 Selenium in surface sediments collected in the RMP program. In post-1998 sampling, concentrations are generally below 0.5 mg/g. There are several exceedances of this value in data collected prior to 1998. *The sampling stations are actually in the Bay near the mouths of these two rivers.

Average selenium concentrations in bottom sediments of the North Bay show spatial variations at the RMP long-term monitoring sites although the total range of concentrations is not large. Sediment selenium concentrations are somewhat lower for the San Joaquin and Sacramento River stations near Mallard Island and the Central Bay stations (below 0.3 μg/g), whereas bottom sediments at sites in Grizzly Bay, San Pablo Bay and Napa River exhibit slightly elevated selenium concentrations (> 0.4 μg/g).

Sediment concentrations from RMP random sampling indicate somewhat larger spatial variation than the long-term sites because these are single point concentrations and not averages. The majority of the sediment samples have concentrations between 0.2 – 0.3 μg/g, while concentrations as high as 1.7 μg/g were also observed. The average for the whole North Bay is 0.25 μg/g.

Selenium concentrations in the bottom sediments are correlated to sediment grain size and organic carbon content. Sediment selenium concentrations were found to be highly related to percent fines < 0.00625 mm and percent total organic carbon (TOC) (Figure 3-10). Relationships between sediment selenium and percent fines and TOC are weaker for the random monitoring sites, however clear positive relationships are still observed. Sites with low sediment selenium concentrations correspond to low percent fines in the sediments and vice versa. Meseck (2002) observed a similar strong relationship between sediment selenium and organic carbon concentrations (r^2 = 0.85). The relationship with TOC suggests that organic carbon, whether as plankton, or as detrital organic matter, plays an important role in the settling and removal of selenium from the water column to the sediments.

As with data in the dissolved and particulate phase, the above discussion provides an understanding of the movement of selenium thorough the NSFB, and insight into the long-term fate and sequestration of selenium from the water column in selected locations. Sediment data, as obtained from deep cores, are usually good records of historical inputs to the system. However, such data have not been reported in the bay, and it is unknown what the historical background concentrations of selenium were.

3.4. PLANKTON AND BACTERIA

Plankton-associated selenium is a subset of the total particulate selenium that is measured in water samples. Although the interactions with the water column are often expressed with an equilibrium partition coefficient, plankton demonstrate more complex behavior that has been established in laboratory studies, including with species of relevance to the NSFB (see discussion in Section 2.5). However, the majority of the data collected from bay water samples is for particulates as a whole rather than as algal fractions. The algal/bacterial contribution is inferred through selenium contents on particles and chlorophyll a concentrations as discussed in Section 3.2. The field data do not allow any examination of the role of algal species in selenium uptake that has been demonstrated in laboratory studies such as Baines and Fisher (2001).

Bacterial and algal uptake of selenium (added as radiolabeled selenite) from waters of the Delta have been quantified through laboratory experiments (Baines et al., 2004). No similar experiments have been reported for waters collected in the NSFB. However because of the close connection between the Delta and the NSFB, especially Suisun Bay, these data are useful to consider. These data show significant uptake of selenite in the dark, and by organisms smaller than a 1 μm, which is associated with bacteria. Bacterial selenium concentrations were found to be about 2.4-13 times higher than the phytoplankton concentrations in this study.

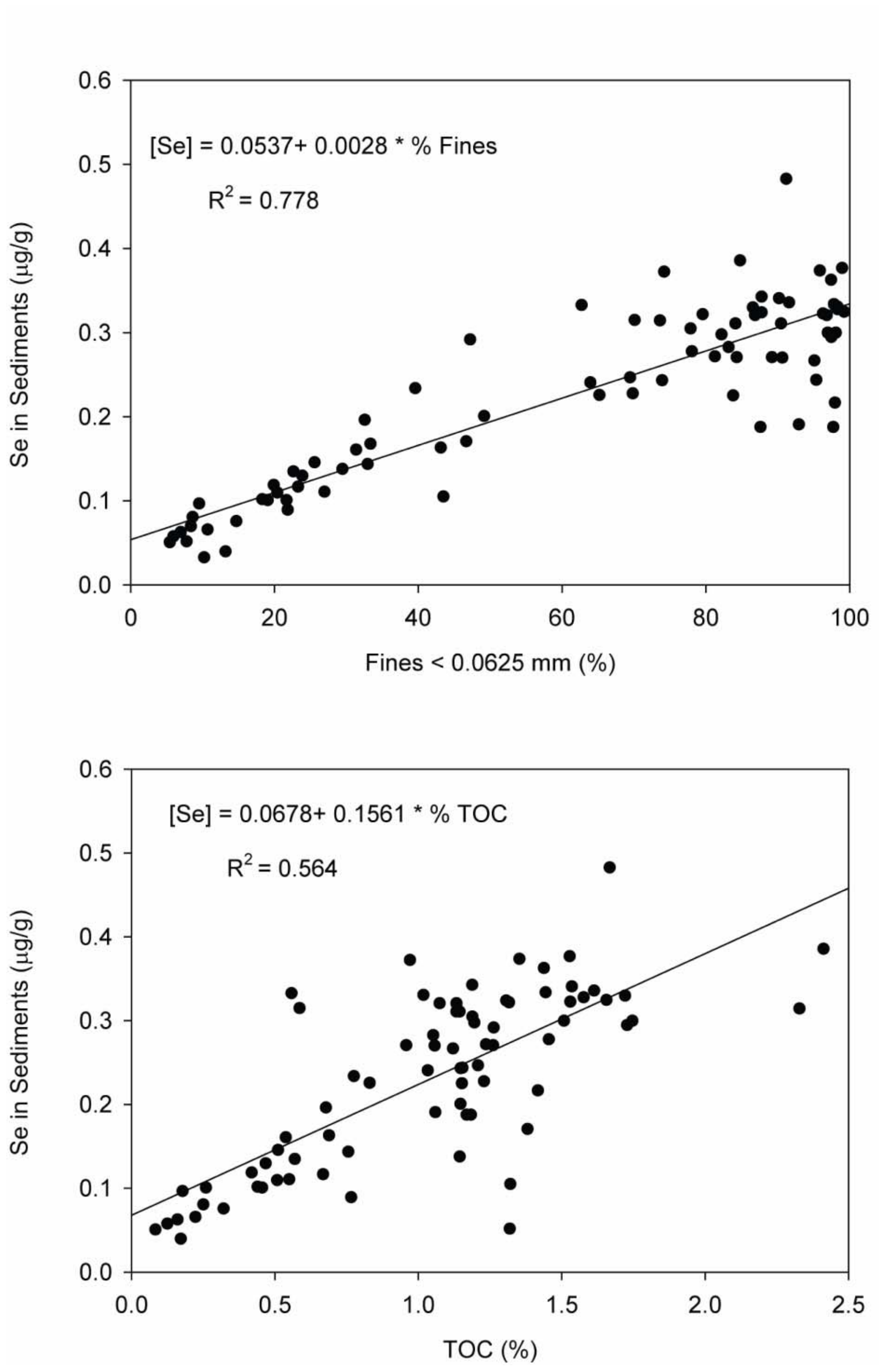


Figure 3-10 Relationship between selenium concentrations in sediments and sediment characteristics at long-term sites (data source: RMP).

Controlled laboratory studies have shown the higher assimilative efficiency of selenium from algal cells in bivalves relative to other particulate forms. Data on plankton and bacteria suggest that this process is even more significant because the concentrations and assimilative capacity are both higher.

3.5. ZOOPLANKTON

Bioaccumulation through zooplankton is a possible pathway for organisms that feed in the water column, such as splittails and striped bass (first demonstrated by Reinfelder and Fisher, 1991; Fisher and Reinfelder, 1991). Zooplankton selenium concentrations in NSFB have been reported by Pukerson et al. (2003) and were collected three times as part of USGS sample cruises in the bay. Zooplankton were collected in 73 µm nets and classified by size. Dry weight selenium concentrations ranged between 1.02 and 6.07 µg/g dry weight. The 73-2000 µm size fraction of zooplankton is shown in Figure 3-11 as a function of location and for the three sample dates (Fall 1998, Spring 1999, and Fall 1999). The data show no strong spatial gradients although there are clear temporal effects, with fall 1999 values being significantly higher than the other two dates. Zooplankton data from November 1999 reported in a separate study (Stewart et al., 2004) are consistent with the high values shown in Figure 3-11 (median concentration ~5 µg/g dry weight).

Concentrations in zooplankton in NSFB show no enrichment compared to other ecosystems in which there is no known selenium contamination. Modeled estimates of zooplankton selenium are supportive of the field information (Schlekat et al., 2004). The predicted concentrations range between 1.5 and 5.4 µg/g and are significantly lower than bivalve concentrations predicted and observed in the bay.

3.6. BIVALVES

Bivalve selenium data in NSFB have been collected by the USGS (Linville et al., 2002; Stewart et al., 2004) and by the RMP (data obtained from SFEI website; Gunther et al., 1998; Lowe et al., 2005). There are differences in the types of data collected by the two monitoring/research programs. The USGS efforts have focused on resident and transplanted bivalves, including *P. amurensis*, whereas the RMP protocol uses only transplanted clams that are left at various stations for a set period, and then analyzed to evaluate the change from initial conditions. The RMP uses different bivalves due to varying salinities in the bay: the clam *Corbicula fluminea* is used in Suisun Bay, the oyster *Crassostrea gigas* is used near Carquinez Strait, and the mussel *Mytilus californianus* is used in San Pablo Bay.

Bivalve selenium data collected by the USGS shows high concentrations and significant enrichment compared to particulate selenium (6 µg/g to 20 µg/g dry weight). The data also show a seasonal trend, with the highest concentrations in late fall (Linville et al., 2002), a period during which certain diving duck predators are very active (Figure 3-12). Comparison with older datasets (Figure 3-13) demonstrates that bivalve concentrations in the bay were higher in the mid-1990s than the mid 1980s, driven by a change in species to *P. amurensis* (Linville et al., 2002), a species that has been shown to bioaccumulate selenium to a greater degree because of higher ingestion rates and higher assimilative efficiencies compared to native species (Lee et al., 2006).

Bivalve uptake of selenium has been studied extensively in the bay. These data are vital to the selenium TMDL because they aggregate water column selenium supply through particulates and are a key step to the bioaccumulation in organisms of most concern (diving ducks and white sturgeon). However, much of the published data dates to 1999 or earlier. There is very little published data on resident bivalves obtained after refinery load reductions in 1998. Existing data suggest that there has been minimal change in concentrations in response to the load changes. Continuing data collection by the USGS, as yet unpublished, may shed more light on the changes in bioaccumulation that have occurred after major reductions in selenium point source discharges.

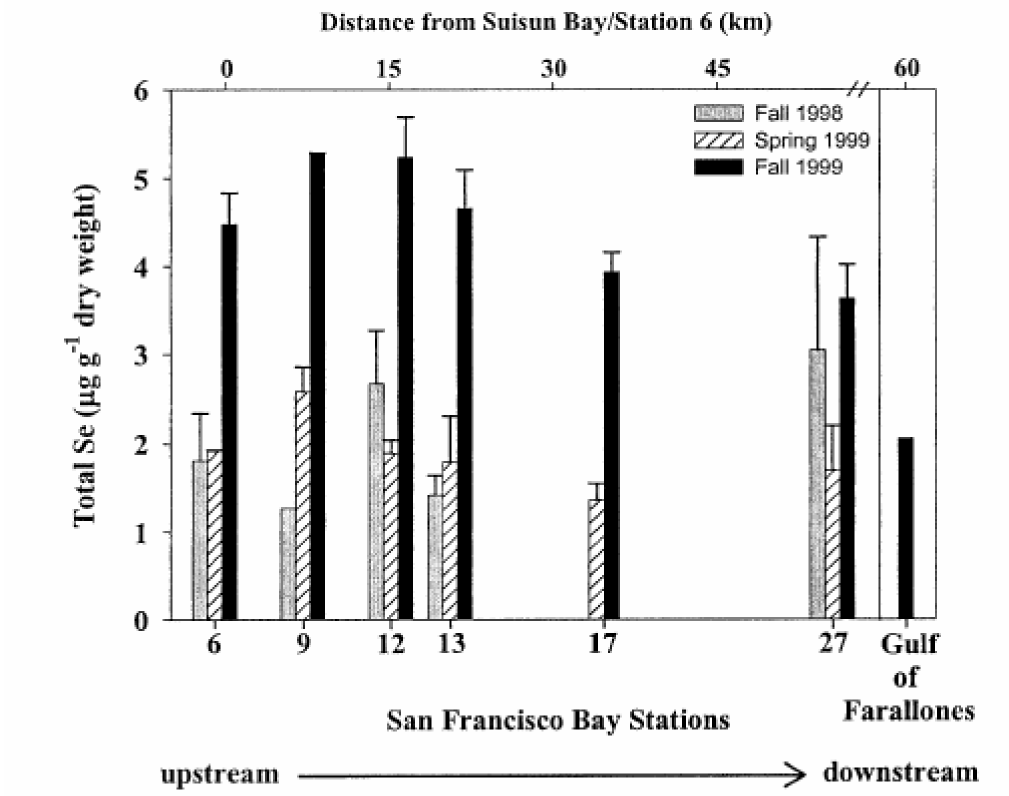


Figure 3-11 Zooplankton data collected in NSFB compared with a reference site in the Gulf of Farallones. Figure reproduced from Pukerson et al. (2003).

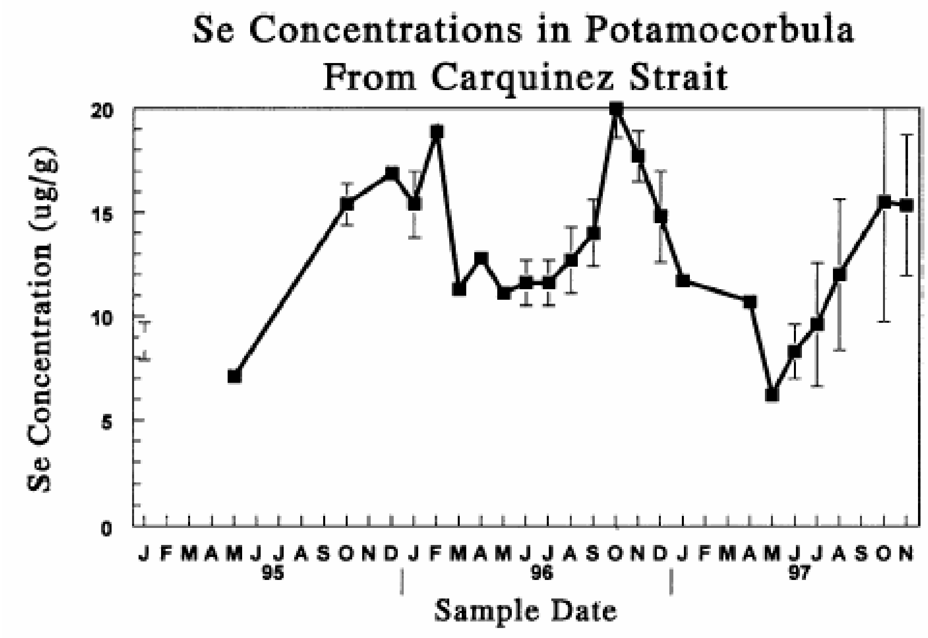


Figure 3-12 P. amurensis selenium concentrations as a function of season in Carquinez Strait (Source: Linville et al., 2002)

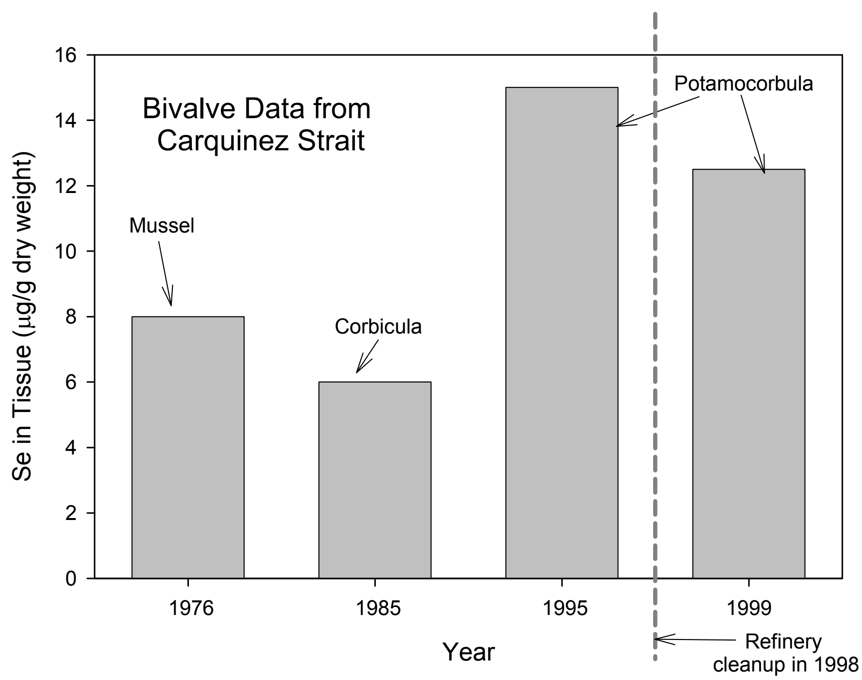
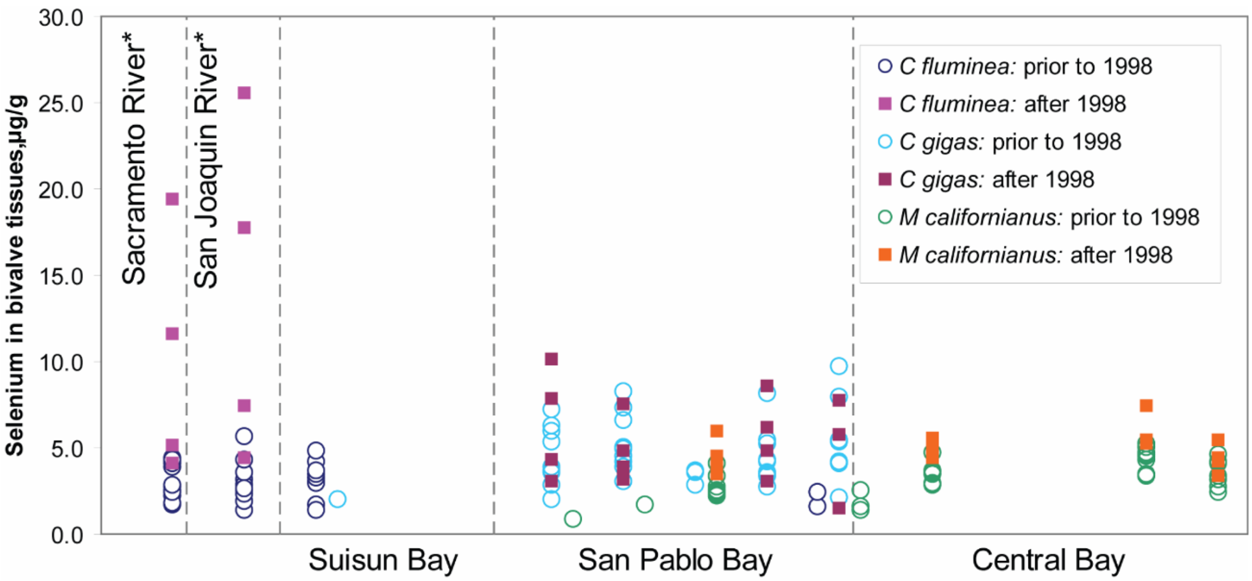


Figure 3-13 Bivalve data in NSFB over three decades. Data from 1976 and 1985 are from Linville et al. (2002) and are originally from older studies. Data from 1995 is from Linville et al. (2002). Data from 1999, following refinery wastewater load reductions, are from Stewart et al. (2004).

Interpretation of transplanted bivalve data is more difficult because of changes in concentration from initial conditions and because of changes in the condition index, which reflects growth and feeding or lack thereof. Spatial and broad temporal (pre-1998 and post-

1998) trends are shown in Figure 3-14. With some exceptions in the Delta stations (identified as Sacramento and San Joaquin River), the data show lower concentrations than in *P. amurensis*, with marginally higher concentrations in San Pablo Bay. There are no clear differences between the pre-1998 and post-1998 data, although it appears that post 1998 data are somewhat higher.

The highest concentrations of sediments and bivalves are plotted in Figure 3-15, along with locations of all the sediment sampling points and the locations of the five active refineries. For the sediments, only two of the eighteen samples shown in the figure were collected after 1995. Six of the eighteen were from rivers: Sacramento, San Joaquin, Petaluma, and Napa River. Many of the high bivalve samples were at the same locations, especially at river locations (11 of 18 samples). Even though locations of samples with high concentrations are similar, the dates of collection are not, but may differ by years. The highest concentrations generally are not near the large refinery point sources, except for Conoco Phillips.

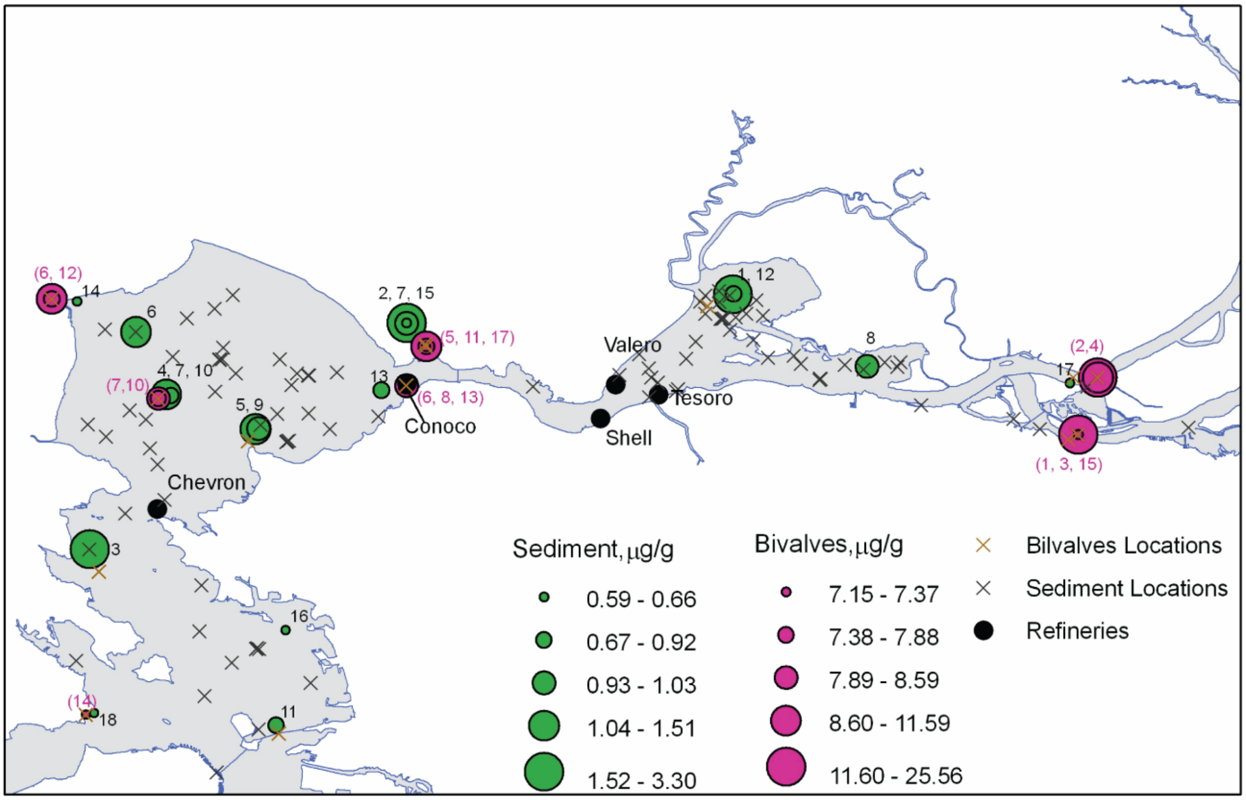


*The sampling stations are actually in the Bay near the mouths of these two rivers

Figure 3-14 Concentrations of selenium in various media throughout the NSFB segregated by time prior to, and subsequent to, 1998 (RMP data)

Temporal trends in transplanted bivalve data are shown in Figure 3-16. Despite decreases in dissolved selenium concentration these trend lines are all positive. Many of the curves appear to show some seasonal differences, again with many of the peaks occurring during the dry seasons. Overall, the finding of an increasing trend with time is counter-intuitive and may highlight processes related to selenium particulate concentrations that have responded differently from dissolved phase concentrations.

In summary, it appears that the resident bivalve data are most useful for evaluation of selenium bioaccumulation, and serve as a direct measure of a dietary concentration of relevance to bioaccumulation in diving ducks and white sturgeon.



Sediments, µg/g

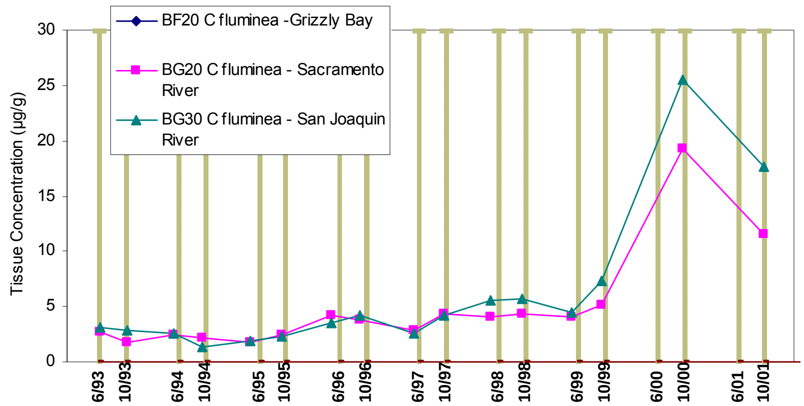
Rank	Site Code	Location	Sample Date	µg/g
1	BF21	Grizzly Bay	09/20/1993	3.300
2	BD50	Napa River	09/21/1993	2.240
3	CB075S	Central Bay	07/29/2004	1.702
4	BD22	San Pablo Bay	09/21/1993	1.510
5	BD31	Pinole Point	09/21/1993	1.270
6	SPB015S	San Pablo Bay	07/28/2004	1.267
7	BD50	Napa River	02/11/1994	1.025
8	BF40	Honker Bay	02/10/1994	1.014
9	BD31	Pinole Point	02/11/1994	0.970
10	BD22	San Pablo Bay	02/11/1994	0.923
11	BC11	Yerba Buena Island	09/22/1993	0.860
12	BF21	Grizzly Bay	02/10/1994	0.843
13	BD41	Davis Point	09/21/1993	0.700
14	BD15	Petaluma River	02/17/1995	0.664
15	BD50	Napa River	08/26/1994	0.664
16	BC41	Point Isabel	02/14/1994	0.618
17	BG20	Sacramento River	09/20/1993	0.610
18	BC21	San Joaquin River	09/22/1993	0.590

Bivalves, µg/g

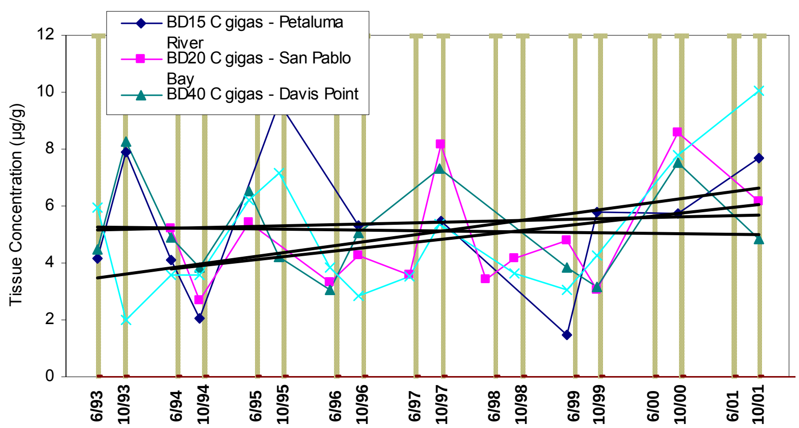
Rank	Bivalve	Site Code	Location	Sample Date	µg/g
1	CFLU	BG30	San Joaquin River	09/22/2000	25.56
2	CFLU	BG20	Sacramento River	09/22/2000	19.34
3	CFLU	BG30	San Joaquin River	09/30/2001	17.66
4	CFLU	BG20	Sacramento River	09/30/2001	11.59
5	CGIG	BD50	Napa River	09/28/2001	10.07
6	CGIG	BD15	Petaluma River	09/13/1995	9.65
7	CGIG	BD20	San Pablo Bay	09/18/2000	8.59
8	CGIG	BD40	Davis Point	10/07/1993	8.25
9	CGIG	BD20	San Pablo Bay	09/25/1997	8.14
10	CGIG	BD15	Petaluma River	10/06/1993	7.88
11	CGIG	BD50	Napa River	09/21/2000	7.80
12	CGIG	BD15	Petaluma River	09/27/2001	7.68
13	CGIG	BD40	Davis Point	09/21/2000	7.52
14	MCAL	BC21	Horseshoe Bay	09/19/2000	7.37
15	CFLU	BG30	San Joaquin River	09/21/1999	7.37
16	CGIG	BD40	Davis Point	09/23/1997	7.29
17	CGIG	BD50	Napa River	09/13/1995	7.15
18	CGIG	BD40	Davis Point	04/26/1995	6.52

Figure 3-15 Locations of sediment and bivalve samples with the highest concentrations plotted (data source: RMP, Cutter and Cutter, 2004)

(a) Samples from Grizzly Bay, Sacramento River, and San Joaquin River



(b) Samples from Petaluma River, San Pablo Bay, Davis Point, and Napa River



(c) Samples from Yerba Buena Island, Horse Shoe Bay, Redrock, and Pinole Point

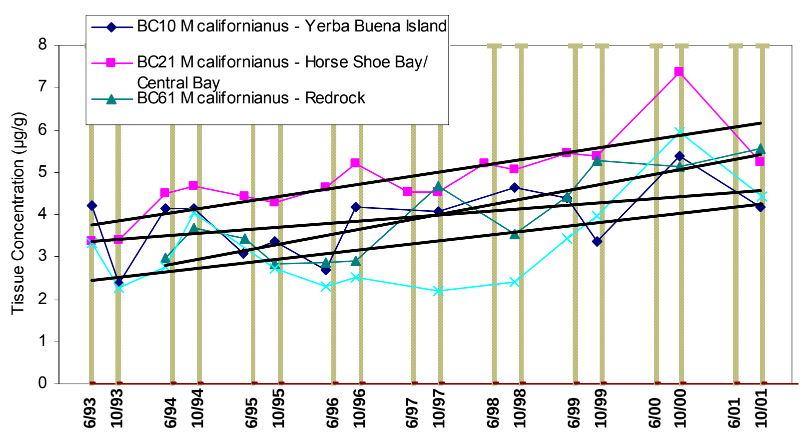


Figure 3-16 Time series and trends of selenium in tissue of transplanted bivalve in NSFB.

3.7. Fish and Birds

Presser and Luoma (2006) provide a detailed discussion of selenium in tissues of birds and fish in the Bay, so only a brief summary is provided here. The Department of Fish and Game conducted extensive sampling of bird and fish species in the Bay from 1986 through 1990 on behalf of the Sate Water Quality Control Board (White et al., 1987, 1988, 1989; Urquhart et al., 1991). Fish samples collected in the Bay were compared against fish samples from Humboldt Bay, a bay with no known sources of selenium. The greatest differences occurred in bottom-feeding fish, and concentrations in San Francisco Bay were found to be 2 to 3 times higher in flesh of bottom feeding fish. However herbivorous fish (such as striped bass) showed little difference in selenium tissue concentrations. Dungeness crabs in Suisun Bay contained a mean concentration of 14 µg/g dwt tissue, compared to 5µg/g dwt in Humboldt Bay (Presser and Luoma, 2006).

The highest concentrations of selenium were found in white sturgeon in the Bay (White et al., 1987). White sturgeon are voracious consumers of *P. amurensis*, which strongly suggests the possibility that selenium tropic transfer via bivalves is an important pathway of selenium exposure. Selenium concentrations in livers of white sturgeon did increase subsequent to the introduction of this bivalve: from an average concentration in liver of 9.2 µg/g-dwt in 1986 to 30 µg/g-dwt in 1989-90. More recent data (1997-2003) report concentrations in muscle tissue alone, and these show a decrease from values in the late-1980s to values more like those in the mid- 1980s, i.e., prior to the invasion of *P. amurensis*. The most recent sturgeon muscle data from San Pablo Bay (2003) are much lower than past measurements, but there are limited data behind this inference (two data points).

Comparatively limited data have been collected in the NSFB following the extensive sampling efforts of the 1980's. Some of these recent sampling results are presented in this section. Data for White sturgeon muscle tissue are shown in Figure 3-17. The data show high concentrations in tissue, but are not sufficient to allow inference of any temporal trends. Recent data for Sacramento splittail and White sturgeon, including muscle and liver concentrations, are shown in Figure 3-18. The data clearly illustrate the dramatic elevation in concentrations caused by the benthic food web dependence of the White sturgeon. The splittail liver data are from the Delta (no NSFB data have been collected in recent years). Finally, a small amount of bird muscle data is shown in Figure 3-19. Contrary to data in particles and bivalves, the very limited bird data shows lower recent concentrations that obtained in the 1980s.

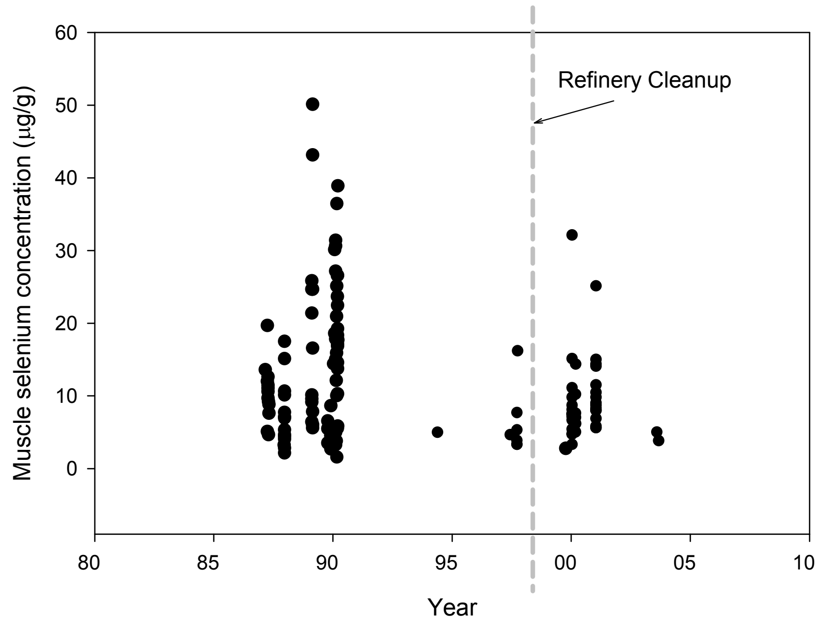


Figure 3-17 Data from NSFB showing selenium in white sturgeon muscle tissue (dry weight basis) as a function of time. Data from Selenium Verification Study (White et al., 1988, 1989, Urquhart et al., 1991), USGS and SFEI.

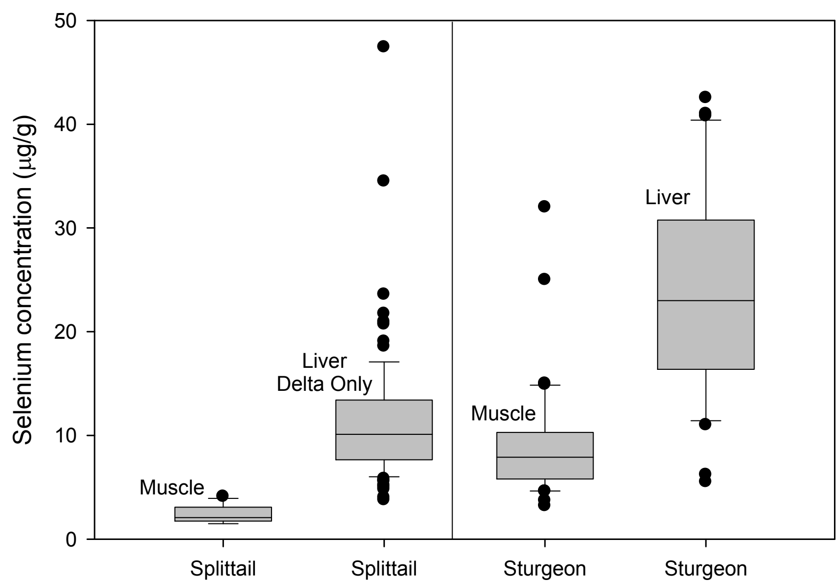


Figure 3-18 Data from NSFB and Delta showing selenium in white sturgeon and splittail livers. Data from USGS and SFEI, collected in 2000 and 2001. Splittail liver data are only from the Delta.

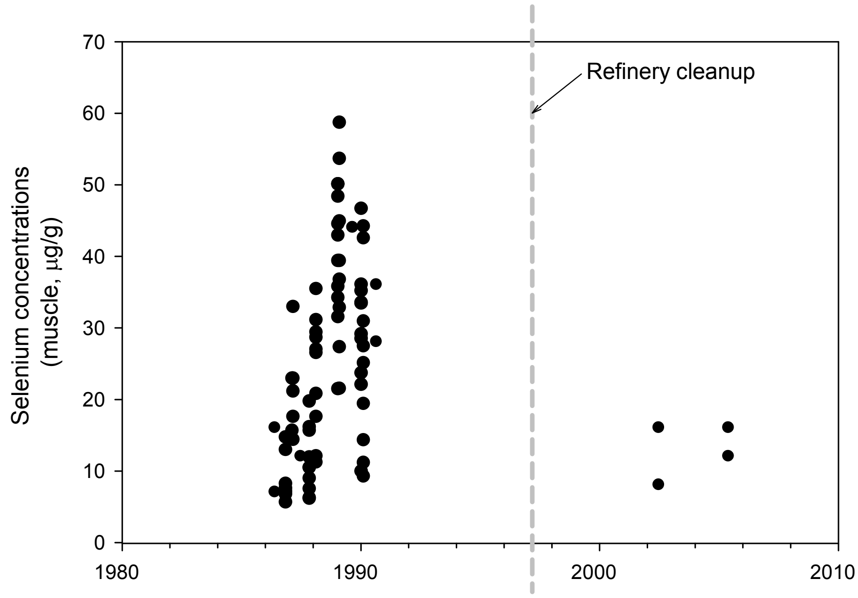


Figure 3-19 Selenium in diving ducks (dry weight basis in muscle tissue) based on data from RMP in 2002 and 2005 (White et al., 1988, 1989; Urquhart et al., 1991; SFEI, 2006).

3.8. Bioconcentration and Bioaccumulation Factors in NSFB

Selenium bioconcentration (direct uptake by algae and bacteria primarily) and bioaccumulation (uptake in higher trophic level organisms through the food web) are both important processes in NSFB. Table 3-3 provides an overview of bioconcentration and bioaccumulation factors, which are ratios of tissue concentrations to water column concentrations. This table was prepared by compiling tissue data and water column data from different sources. These factors are a compact way of representing complex bioaccumulation processes, and illustrate the impact of transfer through various elements of the food web.

Depending on ambient selenium concentrations in the water column, bioconcentration factors by some phytoplankton species can be up to 100,000 (Baines and Fisher, 2001). Assuming a particulate organic matter selenium concentration of 3 µg/g measured in the Bay (similar to concentrations measured in plankton in the Delta; Baines et al., 2004), with a water column selenium concentration of 0.12 µg/L, bioconcentration factor by algae in the NSFB is ~25,000 L/kg. Bivalves typically biomagnify selenium to concentrations higher than those found in the particulate phase (by a factor of 3-4). When these organisms are consumed by predator species such as sturgeon and diving ducks, the selenium is biomagnified further (3-19 times) in the tissues of these animals (Luoma and Presser, 2006).

The estimated bioconcentration factor for plankton is at the higher end compared to values found for freshwaters in North America (24,000 L/kg; EPRI, 2006). BAF values for bivalves and fishes are also higher than those found in freshwaters (Median 7,550 L/Kg in lakes for bivales, 1,000 to 20,000 L/kg for top carnivores in rivers), due to the relatively low selenium concentrations in Bay waters (0.10 µg/L) and the effectiveness of plankton and *P. amurensis* as an assimilator of selenium.

Table 3-3
Selenium concentrations in different media in the bay for post refinery clean up and corresponding bioconcentration/bioaccumulation factors

Media	Concentration	Bioconcentration/bioaccumulation Factors
Water Column	0.10 µg/l (low flow) 0.12 µg/l (high flow)	
Seston	0.73 µg/g (low flow) 0.49 µg/g (high flow)	7,300 L/kg (low flow) 4,800 L/kg (high flow)
Plankton	3 µg/g	25,000 L/kg
Sediment	0.25 µg/g	2,200 L/kg
Bivalve *p. amurensis*	11 µg/g	100,000 L/kg 3 – 4 times plankton concentrations
White Sturgeon (liver)	24.1 µg/g	219, 000 L/kg 2 - 3 times *P. amurensis* concentrations
Zooplankton	4.5 µg/g (low flow) 1.9 µg/g (high flow)	17, 200 - 40, 900 L/kg 0.6 – 1.5 times plankton concentrations
Splittail (liver)	11.4 µg/g	103,600 L/kg 2 - 6 times zooplankton concentrations

4. Relationship to Conceptual Models of Other Contaminants in San Francisco Bay

Over the past decade, a number of conceptual models for contaminants in San Francisco Bay have been developed. Three contaminants of most relevance include: PCBs, mercury, and copper/nickel. This discussion addresses the similarities and differences between the sources, reservoirs, and cycling of the different contaminants and the how the previous conceptual models might influence the evaluation of selenium. None of these conceptual models pertain to NSFB alone; the PCB and mercury models are for the whole bay, and the Cu/Ni model is for Lower South San Francisco Bay.

PCBs: PCBs have no natural sources, and are their presence is largely a legacy of past industrial use. PCBs are strongly associated with sediments and/or particulates in the water column. The primary sources of PCBs in the bay are in the South San Francisco Bay. The existing reservoir of PCBs in sediments is much larger than the annual load into the bay (reservoir >> 10 times annual load). PCBs are taken up through the food web and concentrate strongly in the lipid fractions of tissues. Species of concern for PCBs are white croaker and shiner surfperch. BAFs in fish are $2.2\text{-}5.0\times10^6$ L/Kg for PCBs in the Bay.

Selenium differs from PCBs in the following respects:

- Se has significant natural sources in addition to anthropogenic sources.
- The largest sources of selenium flow into the North Bay rather than the South Bay.
- Selenium exists primarily in the dissolved form, and the reservoir in the upper sediments is a factor of 5-6 times the average annual load.
- Selenium concentrations are regulated by plankton and, once incorporated in cells, are present in various seleno-organic forms. Uptake through clams into diving ducks and white sturgeon results in the highest tissue concentrations. Although bivalves are an important pathway for PCBs, the main source is thought to be sediments.

Mercury: A large portion of the annual mercury loading to the bay originates from historical activities related to mining and use for gold mining in the San Francisco Bay watershed. The largest sources of mercury are non-point sources. Air deposition is a significant source. The existing reservoir of mercury in the upper sediments is much larger than the annual load into the bay (about 10 times annual load). Mercury enrichment in sediments in the bay is much deeper than for PCBs, illustrating the longer history of human alteration of the cycling of this element in the bay watershed. Sediments are important in that they are a major site for methylmercury production. Relatively high concentrations of mercury in the bay are found in piscivorous fish, and wading birds that consume them. BAFs in fish are approximately 1×10^7 L/kg for Hg. Although there are many similarities between mercury and selenium behavior in the bay, the key differences are:

- Unlike mercury, selenium exists primarily in the dissolved form, and partition coefficients to solids are smaller than for mercury.

- The food-web uptake pathways are different, although algae play a role in the initial bioconcentration for both elements. In general, algae do not appear to regulate for mercury uptake in the manner they do for selenium.
- Sediments, although a significant reservoir of selenium, do not play a major role in the production of a more toxic or bioaccumulative form of selenium, in a manner similar to that of methylmercury production.

Copper/Nickel: The primary concern with copper and nickel is adverse impacts to algae at the base of the food web, with possible impacts on higher trophic level organisms. Unlike mercury, PCBs, and selenium, high concentrations in fish and wildlife have not been reported in the bay, and only data from bivalves are available. Both copper and nickel are strongly particle-associated, and, in the Lower South Bay, the existing reservoir in sediments is far larger in the annual loads (>~100 times). Similar to selenium, algae regulate the uptake of copper and nickel, and the bioconcentration factors are dependent upon ambient concentrations. The primary differences with selenium are:

- Higher partition coefficients to particulates, and more present in particle-associated form in the water column.
- Bioaccumulation into higher trophic level organisms is of less concern than impacts to the primary producers.

Although past work with bioaccumulative contaminants in the bay will be a rich source of information in developing the selenium TMDL, there are key differences in the geographic distribution and nature of the sources, as well as the particle association and bioaccumulation of selenium. Subsequent work on the selenium TMDL, including modeling and/or possible corrective actions, may well be substantially different than what has been developed for previous TMDL efforts in San Francisco Bay.

5. SUMMARY

Selenium exists in the +VI (selenate), +IV (selenite), 0 (elemental), and –II (selenide) oxidation states in the dissolved and particulate phases. The biotic uptake and toxicity of selenium depends both on concentrations and chemical speciation, with selenite being the most bioavailable to algae and microbes.

Selenium is discharged into the NSFB primarily from the Sacramento and San Joaquin Rivers, from five petroleum refineries, and from other local point and non-point sources. There are known areas of natural selenium enrichment in the watershed that drains into NSFB, however, anthropogenic activities, such as irrigation in arid and semi-arid areas with seleniferous soils, may exacerbate these loads.

The mechanisms of selenium bioaccumulation have been elucidated through laboratory and field research over the past three decades. Although a portion of selenium entering the bay is in particulate form, most of it is in the dissolved form. Both dissolved and particulate selenium can exist as different species that affect their cycling and bioavailability. Dissolved selenium can be taken up and bioconcentrated by algae and bacteria in the water column and add to the supply of particulate selenium. Erosion from the sediment bed can also be a source of particulate selenium to the water column. Because of the preferential partitioning of some forms of selenium onto particles (both organic and inorganic), particles are a comparatively rich source of selenium to organisms that consume them. Filter-feeding benthic organisms such as bivalves ingest and assimilate the particulate forms of selenium at different efficiencies depending on the type of particulate material. Direct ingestion of dissolved selenium is minimal for organisms besides plankton and bacteria. Bivalves typically biomagnify selenium to concentrations higher than found in the particulate phase. When these organisms are consumed by predator species such as sturgeon and diving ducks, the selenium is biomagnified further in the tissues of these animals. Algal and bacterial-associated selenium can also enter the food chain through a non-benthic pathway, i.e., through zooplankton that feed on these organisms, and through consumer organisms that feed on zooplankton.

Despite the mechanistic knowledge of selenium bioaccumulation summarized here, there are still many uncertainties in predicting future concentrations of selenium in tissues, given a set of internal and external loads. Building on the preceding sections, a summary of the bioaccumulation processes and the key uncertainties that affect the TMDL are presented in Figure 5-1. The key uncertainties range from, for example, changing speciation and loads in response to hydrology, variable algal uptake and abundance, variable bioconcentration in benthic species, and bioaccumulation in higher predator species. The impact of these uncertainties on the TMDL need to be addressed in future work through modeling, and in some limited instances, through additional data collection. This penultimate set of items in this figure relate previous findings to key questions outlined in the next section. Also identified are the literature sources upon which this summary is based.

Summary of Selenium Bioaccumulation and Key Uncertainties that Affect the TMDL

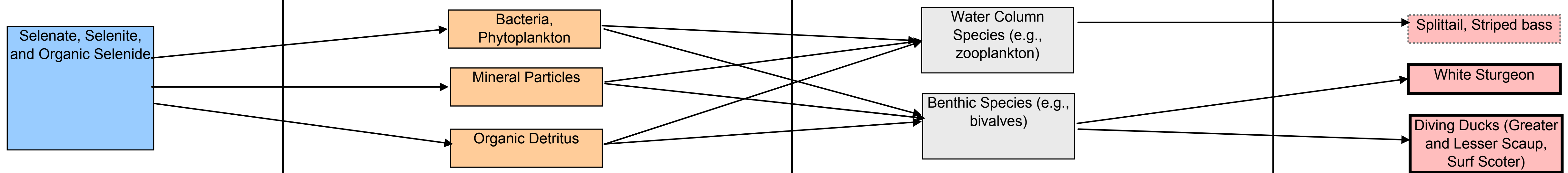
	Dissolved	Particulate	Prey Items	Predators
Selenium in Different Compartments				
State of Knowledge	Most selenium in the water column occurs in the dissolved form (often greater than 90%). Conversion to particulate form, and thus bioavailability, varies by selenium speciation. Concentrations and speciation change with season and with the volume of rainfall during the wet season.	Selenium concentrations are highest in the organic phases (whether live cells or detritus) Selenium in mineral particles are lower than organic particles and overall particulate selenium concentrations are lower when there is a greater proportion of mineral particles. Algal species regulate selenium uptake and may result in similar cellular concentrations even when ambient concentrations change significantly. Algal selenium uptake varies significantly dependening on algal species. Bacterial uptake of selenium may also occur and result in higher cellular concentrations although data are limited.	Although uptake in prey items can be represented by a simple function, there are several variables, especially feeding rate, assimiliative efficiency, and loss rate, that make a significant difference to the prey tissue concentrations. The variables that explain uptake are a function of the species of interest and of the particulate form of selenium. Selenium in living algal cells is found to be more bioavailable than elemental selenium. Published bivalve data show some spatial patterns, but there are differences in behavior among resident and transplanted species. For consideration of actual dietary exposure to higher trophic levels, resident clam data may be most useful. Zooplankton data in the bay are limited although they do not show significant spatial variations, and are similar to concentrations in background locations.	Species dependent on the benthic food web, such as diving ducks and white sturgeon, are most at risk. Based on a limited amount of data, much of it from the 1980s Selenium Verification Study, predator selenium concentrations are generally presented as a linear function of selenium concentration in prey items. There is little direct information on the assimilative efficiency of selenium from different prey items.
Key Factors for TMDL Analysis	Speciation data needed for accurate understanding of uptake, especially in response to changing hydrologic conditions. Speciation data shows a decline in selenite concentrations after refinery cleanup in mid-1998. No speciation data available after 1999.	The bioavailability of different particulate forms varies, with algal selenium being more bioavailable than other forms. Particulate selenium data available for select years, most recently for 1999. In recent years algal abundance, as measured through chlorophyll a levels, in NSFB have increased. No information on background selenium inputs to the NSFB.	Bivalve uptake of selenium is primarily through particulates. Different bivalve species have different uptake rates. Bivalve data are not available after 1999. Prior data show stable concentrations in the late 1990s.	Limited recent tissue concentration data on predator species. Most data show similar results over the late 1990s, although a small amount of diving duck muscle tisse data suggest a small decrease.
Data Sources	Cutter and Cutter, 2004; Doblin et al., 2006; Regional Monitoring Program in San Francisco Bay	Baines and Fisher, 2001; Hogue et al., 2001; Cloern et al., 1992; Cloern et al., 2007	Regional Monitoring Program in San Francisco Bay; Linville et al., 2002; Stewart et al., 2004; Luoma and Rainbow, 2005; Luoma et al., 1992; Schlekat et al., 2002	White et al., 1987, 1988, 1989; Luoma and Presser, 2006; SFEI 2006

Figure 5-1. A summary of the current state of knowledge of selenium bioaccumulation in NSFB, and the key factors in the TMDL analysis. Also shown are the data sources and the relationship to questions discussed in the next section.

6. Key Uncertainties to be Evaluated in Future Work

The information presented here, and the underlying published research, although extensive, nonetheless identifies some information gaps that need to be addressed through future modeling or analysis for the selenium TMDL. Key observations on current data and trends are summarized, and data gaps are identified for future work for this TMDL.

1. **Chemical Speciation**. Both dissolved and particulate selenium can exist as different chemical forms (or species) that affect their cycling, interchange, and bioavailability. Dissolved selenium can be taken up and sequestered by phytoplankton and bacteria to a level hundreds or thousands of times higher than concentrations in the water column. Particulate selenium, whether as part of algal tissue, or associated with organic or mineral matter, is the form that is most likely to be taken up by organisms such as zooplankton, and benthic filter feeders such as bivalves.

   All available data on aqueous selenium concentrations since 1999 in NSFB are total selenium measurements. The likelihood of changes in the dissolved and particulate selenium concentrations and the chemical form of selenium in the aqueous phase from changes in the selenium sources to NSFB is substantial. The lack of these data is an important data gap.

5. **Phytoplankton Community Structure**. Laboratory data show the dramatic effect of algal species on selenium uptake. Given the significance of algal bioconcentration in the overall bioaccumulation process, the impacts of these changes need to be assessed in future years.

   Changes in phytoplankton species composition in the bay change with season and over the years and the effect on the uptake of selenium needs to be quantified.

3. **Bivalve Populations**. There has been an increase in phytoplankton productivity to levels seen prior to the *Potamocorbula amurensis* invasion in the mid-1980s. A hypothesis explaining this finding is that there has been an increase in predators for bivalves that have suppressed phytoplankton grazing. In the recent past, it has been thought that the invasion of *P. amurensis* could adversely affect selenium levels in higher trophic levels because of the ability of *P. amurensis* to bioaccumulate it to higher levels than native species.

   Bivalves are a singularly important link in the observed bioaccumulation of selenium in fish and birds in NSFB. Changes in the abundance of P. amurensis and other bivalve species may affect the levels of bioaccumulation in the future. Additional information is needed on the size and distribution of P. amurensis and other bivalve populations.

4. **Bioaccumulation in Fish and Birds**. The impairment determination for NSFB is principally due to elevated selenium concentrations in fish and waterfowl, and the numeric target for the TMDL is likely to be based on fish tissue concentrations. Yet there is limited recent tissue concentration data on fish and avian species.

   Additional data on tissue concentrations by species and life stage needs to be collected.

7. References

Abu-Saba, K. and S. Ogle. 2005. Selenium in San Francisco Bay: Conceptual Model/Impairment Assessment. Prepared for Clean Estuary Partnership.

Alpine, A.A., Cloern, J.E., 1992. Seasonal changes in the spatial distribution of phytoplankton in small, temperate-zone lakes. J. Plankton Res. 14, 1017-1024.

Baines, S.B., Fisher, N.S. 2001. Interspecific differences in the bioconcentration of selenite by phytoplankton and their ecological implications. Marine Ecology Progress Series, 213: 1-12.

Bowie, G.L., Sanders, J.G., Riedel, G.F., Gilmour, C.C., Breitburg, D.L., Cutter, G.A., Porcella, D.B. 1996. Assessing selenium cycling and accumulation in aquatic ecosystems. Water, Air and Soil Pollution 90: 93-104.

Cloern, J.E., Alpine, A.E., Cole, B.E., and Heller, T. 1992. Seasonal changes in the spatial distribution of phytoplankton in small, temperate-zone lakes. Journal of Plankton Research 14: 1017-1024.

Cloern, J.E., Jassby, A.D., Schraga, T.S., and Dallas, K.L., 2006. What is causing the phytoplankton increase in San Francisco Bay? In The Pulse of the Estuary—Monitoring and managing water quality in the San Francisco Estuary: San Francisco Estuary Institute Annual Report 2006, P. 62-70.

Cloern, J.E., A.D. Jassby, J.K. Thompson, and K.A. Heib. 2007. A cold phase of the East Pacific triggers new phytoplankton blooms in San Francisco Bay, Proceedings of the National Academy of Sciences, Vol. 104, No. 47, pp. 18561-18565.

Cutter, G.A., and L.S. Cutter. 2004. Selenium Biogeochemistry in the San Francisco Bay Estuary: Changes in Water Column Behavior. Estuarine Coastal Shelf Science, 61:463-476.

Doblin, M.A., Baines, S.B., Cutter, L.S. and Cutter, G.A., 2006, Sources and biogeochemical cycling of particulate selenium in the San Francisco Bay estuary: Estuarine, Coastal, and Shelf Science, v. 67, p. 681-694.

EPRI (Electric Power Research Institute). 2006. Fate and effects of selenium in lentic and lotic systems. EPRI, Palo, Alto, CA: 2006. 1005315.

EPA (U.S. Environmental Protection Agency). 2004. Aquatic life water quality criteria for selenium. Draft.

Gunther, A.J., Davis, J.A., Hardin, D.D., Gold, J, Bell, D., Crick, J.R., Scelfo, G.M., Sericano, J., and Stephenson, M. 1999. Marine Pollution Bulletin, Vol. 38, No. 3, pp. 170-181.

Hogue, V.E., F.P. Wilkerson, R.C. Dugdale, and A. Marchi. 2001. Phytoplankton and nutrient dynamics in Suisun, San Pablo, and Central Bays, IEP Newsletter, Volume 14, No. 4, pp. 35-41.

Lee, B.G., J.S. Lee, and S.N. Luoma. 2006. Comparison of selenium bioaccumulation in the clams Corbicula fluminea and Potamocorbula amurensis: a bioenergetic modeling approach. Environmental Toxicology and Chemistry, Vol. 25, No. 7, pp 1933-1940.

Linville, R. G., Luoma, S.N., Cutter, L.S., and Cutter, G.A., 2002 , Increased selenium threat as a result of invasion of the exotic bivalve Potamocorbula amurensis into the San Francisco Bay-Delta: Aquatic Toxicology, v. 57, no. 1-2, p. 51-64.

Lowe, S. B. Thompson, R. Hoenicke, J. Leatherbarrow. 2005. Re-design Process of the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) Status & Trends Monitoring Component for Water and Sediment, SFEI Technical Report.

Luoma, S.N., Johns, C. Fisher, N.S., Steinberg, N.A., Oremland, R.S., and Reinfelder, J.R. 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. Environmental Science Technology 1992 (26): 485-491.

Luoma, S. N. and Rainbow, P.S., 2005, Why is metal bioaccumulation so variable? Biodynamics as a unifying concept: Environmental Science and Technology, v. 39, no. 7, p. 1921-1931.

McDonald, E.T. and R.T. Cheng. 1996. A Numerical Model of Sediment Transport Applied to San Francisco Bay, California. Journal of Marine Environmental Engineering, 4:1-41.

Meseck, S.L. 2002. Modeling the biogeochemical cycle of selenium in the San Francisco Bay. A dissertation submitted to the faculty of Old Dominion University in partial fulfillment of the Degree of Doctor of Philosophy

Meseck, S.L. and G.A. Cutter. 2006. Evaluating the Biogeochemical Cycle of Selenium in San Francisco Bay through Modeling. Limnology and Oceanography, 51(5), pp. 2018-2032.

Pukerson, D.G., Doblin, M.A., Bollens, S.M., Luoma, S.N., Cutter, G.A. 2003. Selenium in San Francisco Bay zooplankton: potential effects of hydrodynamics and food web interactions. Estuaries 26: 956-969.

Porterfield, G. 1980. Sediment Transport of Streams Tributary to San Francisco, San Pablo, and Suisun Bays, California, 1909-66. U.S. Geological Survey, Water Resources Investigations, 80-64.

Presser, T. and S. Luoma. 2006. Forecasting Selenium Discharges to the San Francisco Bay-Delta Estuary: Ecological Effects of a Proposed San Luis Drain Extension. Professional Paper 1646. U.S. Geological Survey.

Riedel G.F., Ferrier, D.P., and Sanders, J.G. 1991. Uptake of selenium by freshwater phytoplankton. Water, Air and Soil Pollution 57-58: 23-30.

Riedel, G.F., Sanders, J.G., and C.C. Gilmour. 1996. Uptake, transformation, and impact of selenium in freshwater phytoplankton and bacterioplankton communities. Aquat. Microb. Ecol. 11, 43-51.

Reinfelder, J.R., Fisher, N.S., Luoma, S.N., Nichols, J.W., Wang, W.-X. 1998. Trace element trophic transfer in aquatic organisms: A critique of the kinetic model approach. The Science of the Total Environment 219: 117-135.

Schlekat, C.E., Dowdle, P.R., Lee, B., Luoma, S.N., Oremland, R.S., 2000. Bioavailability of particle-associated Se to the bivalve Potamocorbula amurensis. Environ. Sci. and Technol. 34, 4504-4510.

Schlekat, C.E., Pukerson, D.G., and Luoma, S.N. 2004. Modeling selenium bioaccumulation through anthropod food webs in San Francisco Bay, California, USA. Environmental Toxicology and Chemistry, 23 (12): 3003-3010.

SFEI (San Francisco Estuary Institute). 2006. Pulse of the Estuary.

Stewart, R.S., Luoma, S.N., Schlekat, C.E., Doblin, M.A., and Hieb, K.A., 2004, Food web pathway determines how selenium affects ecosystems: A San Francisco Bay case study: Environmental Science and Technology, v. 38, no. 17, p. 4519-4526.

Thomson-Becker, E.A. and S.N. Luoma. 1985. Temporal Fluctuations in Grain Size, Organic Materials and Iron Concentrations in Intertidal Surface Sediment of San Francisco Bay. Hydrobiologia, 129:91-107.

Urquhart, K.A.F., K. Regalado et al. 1991. Selenium verification study, 1988-1990 (report 91-2-WQWR), A report from the California Department of Fish and Game to the California State Water Resources Control Board; California Sate Water Resources Control Board Sacramento, California, 94 p. and 7 appendices.

Velinsky, D.J., and Cutter, G.A., 1991, Geochemistry of selenium in a coastal salt marsh: Geochimica et Cosmochimica Acta, v. 55, p.179-191.

White, J.R., Hofmann, P.S., Hammond, D., and S. Baumgartner. 1987. Selenium verification study, 1986, A report from the California Department of Fish and Game to the California Sate Water Resources Control Board: California Sate Water Resources Control board, Sacramento, California, 79p. and 9 appendices.

White, J.R., Hofmann, P.S., Hammond, D., and S. Baumgartner. 1988. Selenium verification study, 1986-1987, A report from the California Department of Fish and Game to the California Sate Water Resources Control Board: California Sate Water Resources Control Board Sacramento, California, 60 p. and 8 appendices.

White, J.R., Hofmann, P.S., Urquhart, K.A.F., Hammond D., and S. Baumgartner. 1989. Selenium verification study, 1987-88, A report from the California Department of Fish and Game to the California State Water Resources Control Board: California State Water Resources Control Board, Sacramento, California, 81 p. and 11 appendices.